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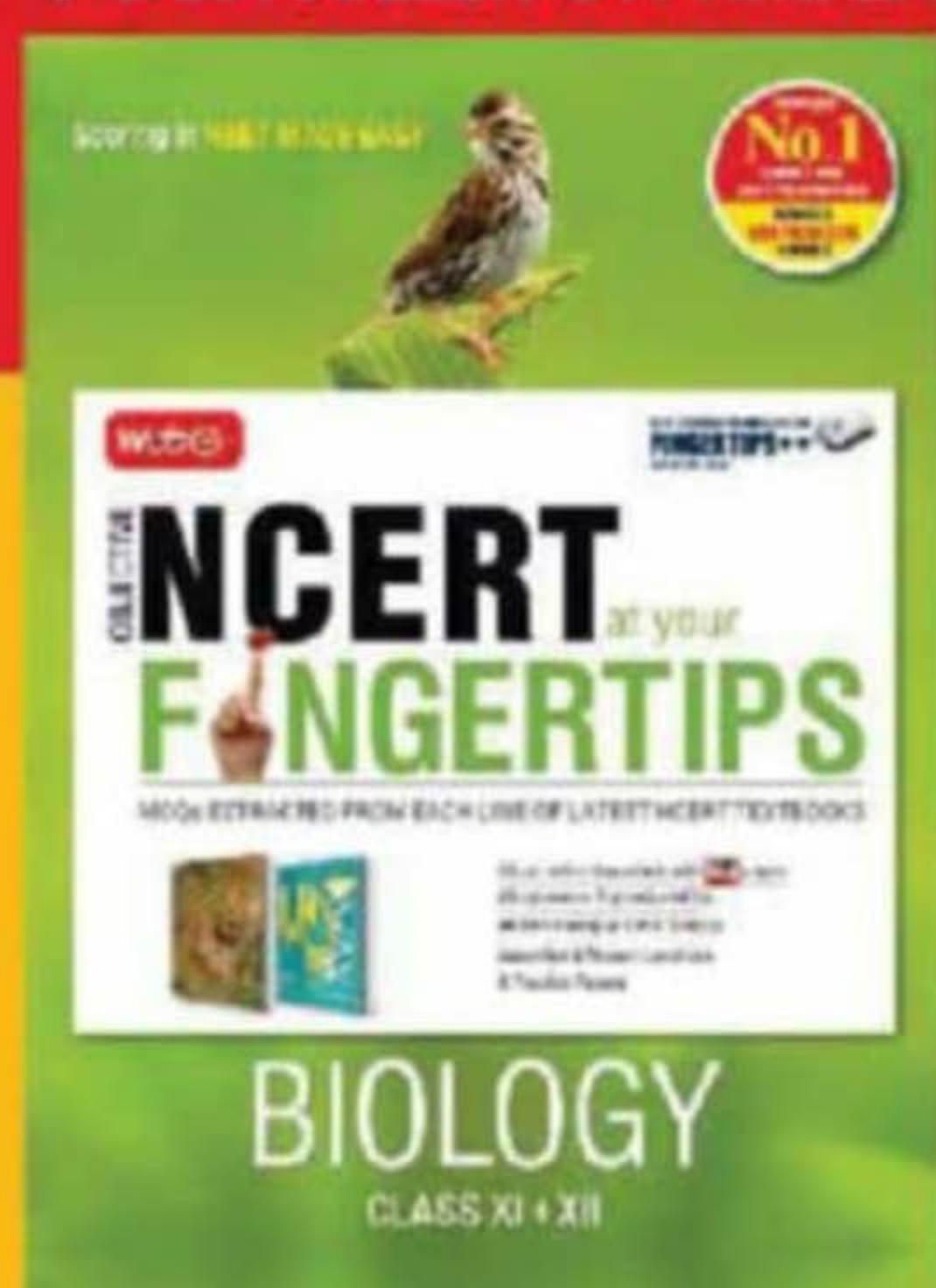
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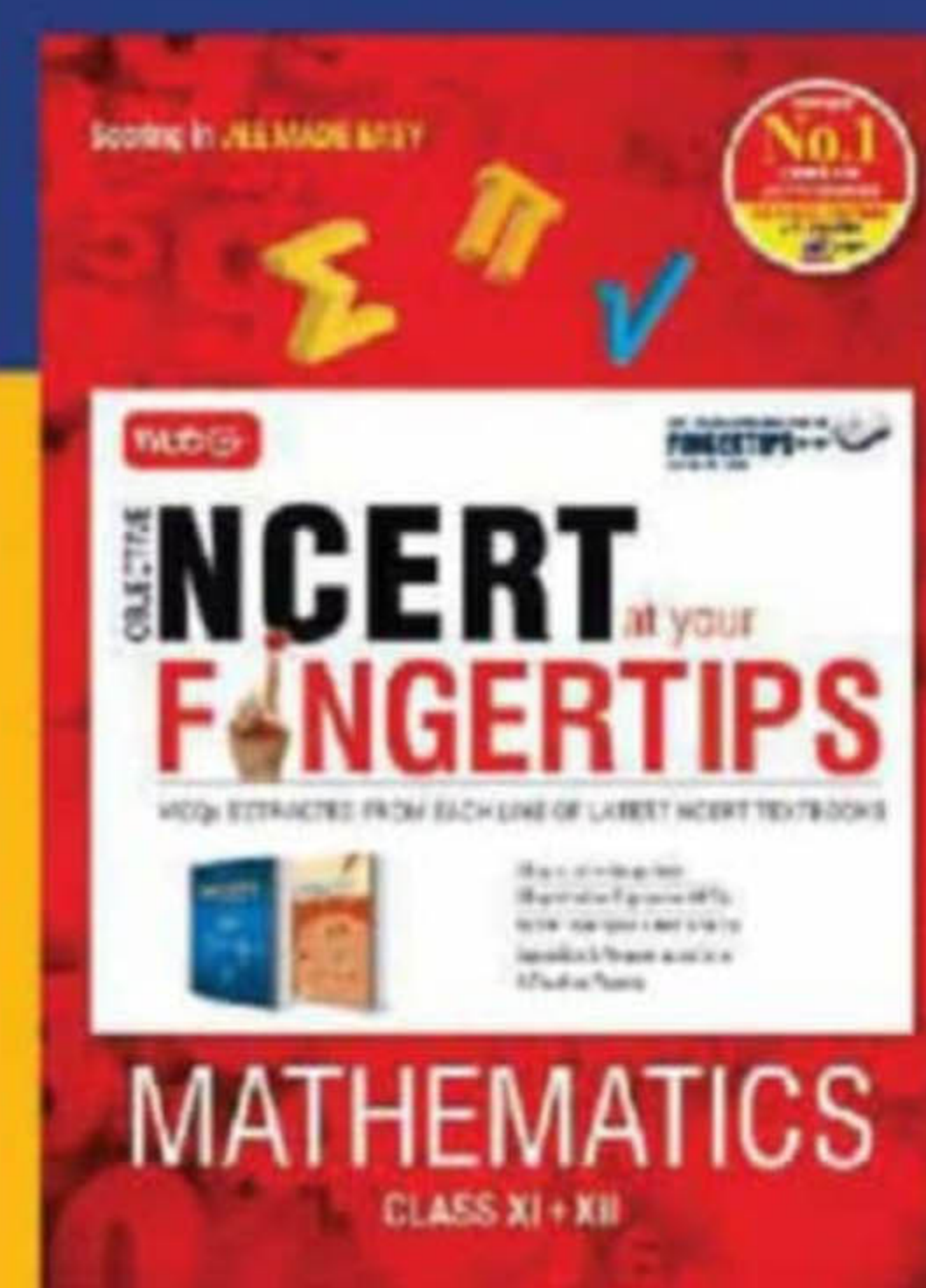
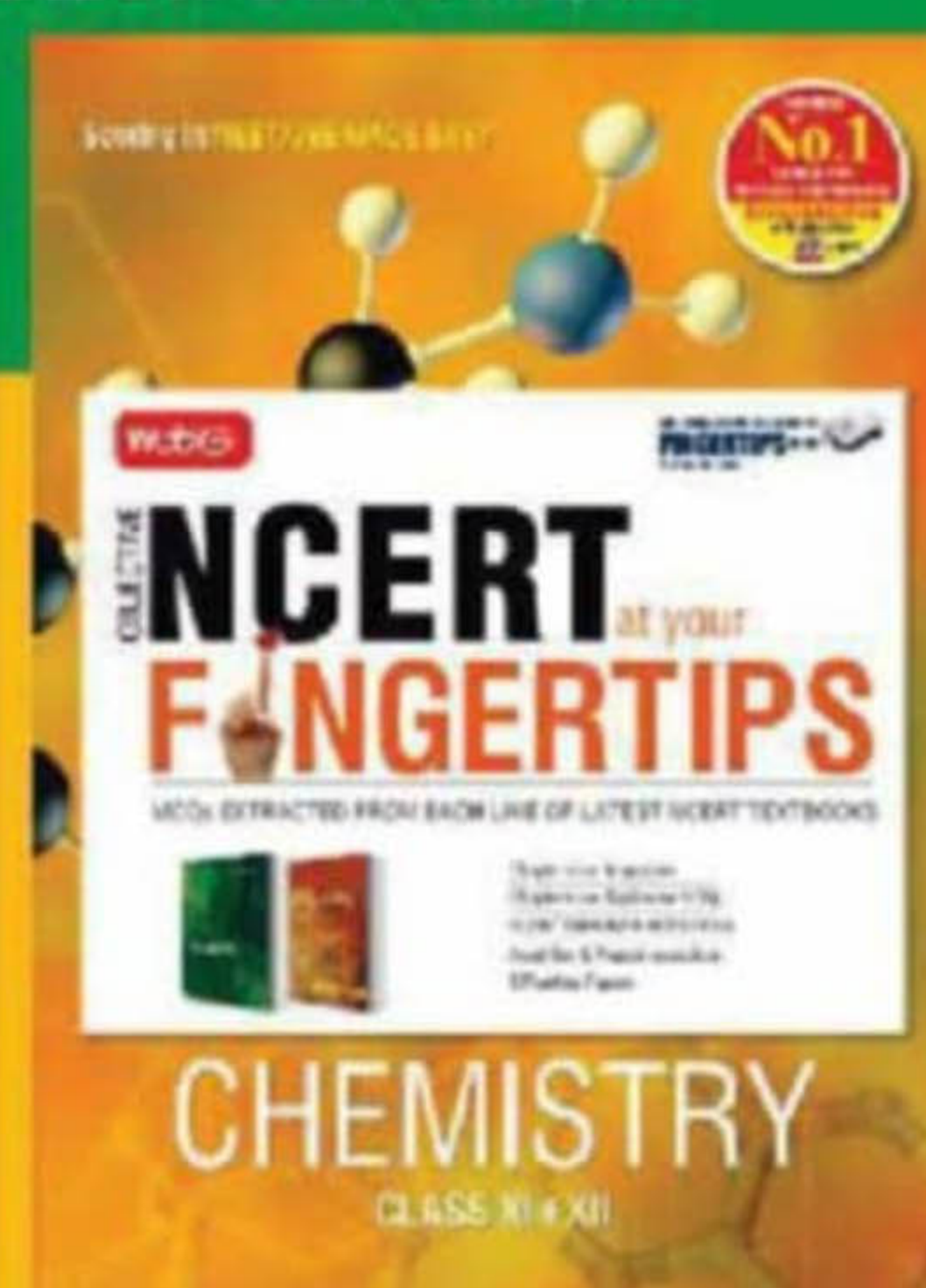
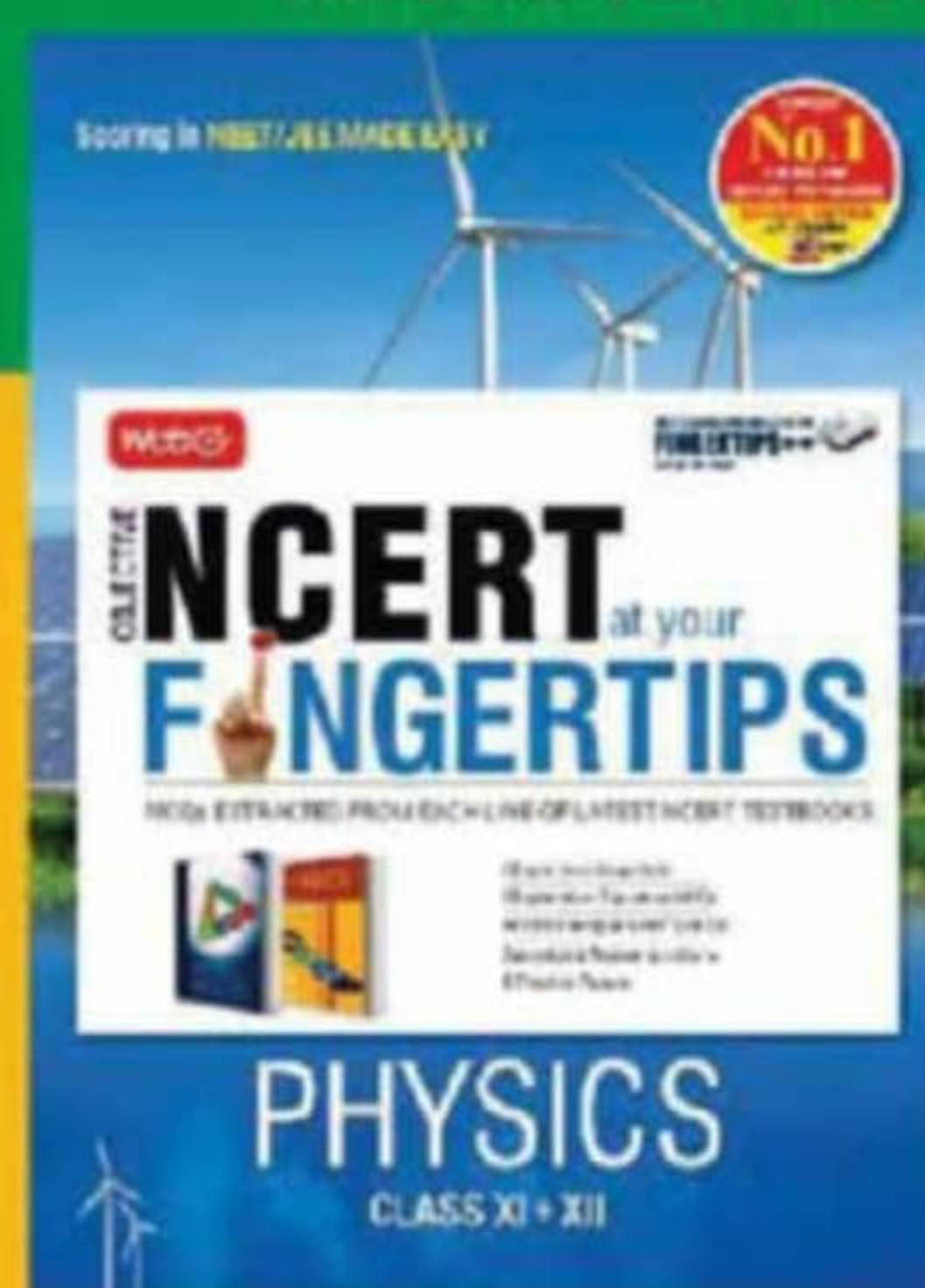
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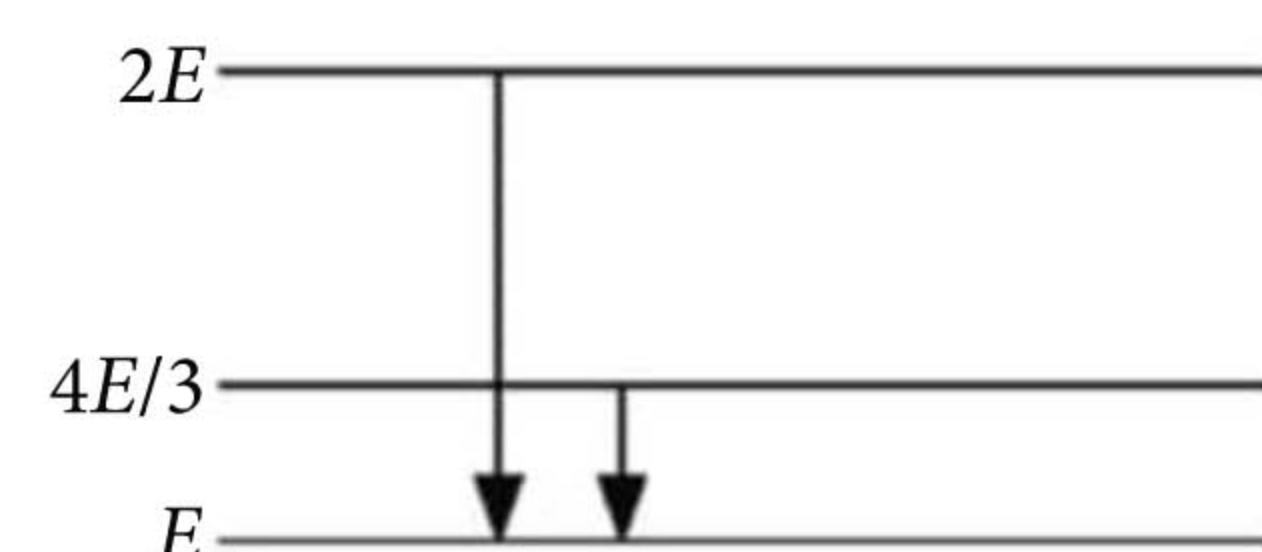
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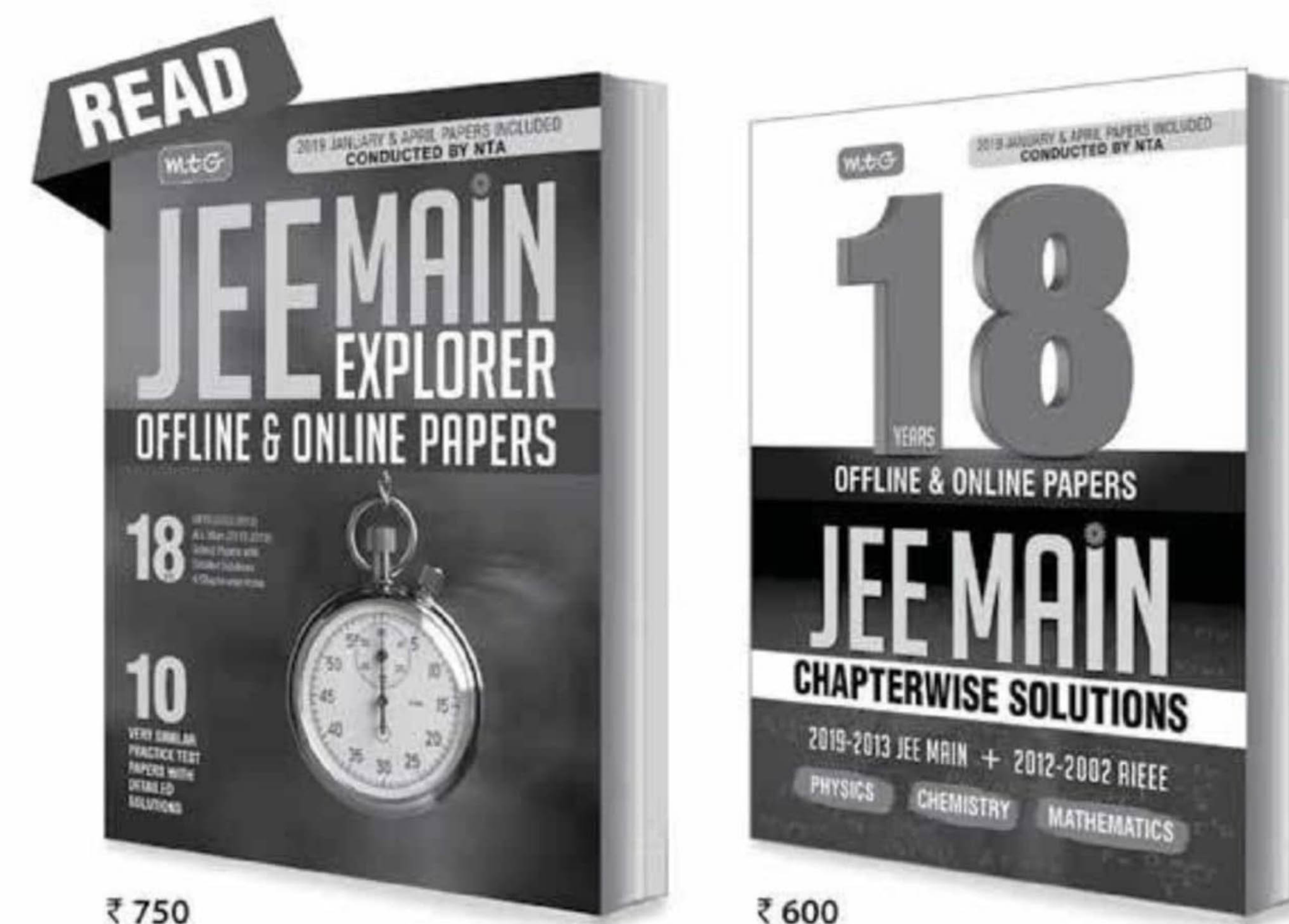
Only One Option Correct Type

- If equal masses of SO_2 and O_2 are placed in a flask at STP then choose the incorrect statement about it.
 - The number of molecules of O_2 is more than that of SO_2 .
 - Volume occupied at STP is more for O_2 than that of SO_2 .
 - The ratio of number of atoms of SO_2 and O_2 is 3 : 4.
 - Moles of SO_2 is greater than the moles of O_2 .
- What is false about H_2O_2 ?
 - Acts as both oxidising and reducing agent.
 - Both OH bonds lie in the same plane.
 - Pale blue liquid.
 - Can be reduced by O_3 .
- The following figure indicates the energy levels of a certain atom. When the system moves from $2E$ level to E level, a photon of wavelength λ is emitted. The wavelength of the photon produced during the transition from level $4E/3$ to level E is



- $\frac{\lambda}{3}$ (b) $\frac{3\lambda}{4}$ (c) $\frac{4\lambda}{3}$ (d) 3λ
- 100 cm^3 of a given sample of H_2O_2 gives 1000 cm^3 of O_2 at S.T.P. The given sample is
 - 10 volume H_2O_2
 - 90% H_2O_2
 - 10% H_2O_2
 - 100 volume H_2O_2
- What will be the pH of the resulting solution? 100 mL of 0.1 M MgCl_2 solution is mixed with 100 mL of 0.2 M NaOH solution. (K_{sp} for $\text{Mg}(\text{OH})_2 = 12 \times 10^{-12}$)
 - 11.45
 - 7.56
 - 12.5
 - 10.45
- The chemical reactions involve in the ammonia-soda process are represented as follows : $2\text{NaCl} + \text{CaCO}_3 \longrightarrow \text{Na}_2\text{CO}_3 + \text{CaCl}_2$
In the following reaction,
 $\text{CaCO}_3 \xrightarrow{\Delta} [\text{A}] + [\text{B}]$
 $\text{NaCl} + \text{NH}_3 + [\text{B}] + \text{H}_2\text{O} \longrightarrow [\text{C}] + [\text{D}]$
 $2[\text{C}] \xrightarrow{\Delta} \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} + [\text{B}]$
Identify A to D.
 - A- $\text{Ca}(\text{OH})_2$; B- CaO ; C- NH_4Cl ; D- NaHCO_3
 - A- CaO ; B- CO_2 ; C- NaHCO_3 ; D- NH_4Cl
 - A- CO_2 ; B- CaOCl_2 ; C- NaHCO_3 ; D- NaCl
 - A- CaCl_2 ; B- CO_2 ; C- Na_2CO_3 ; D- NaOH

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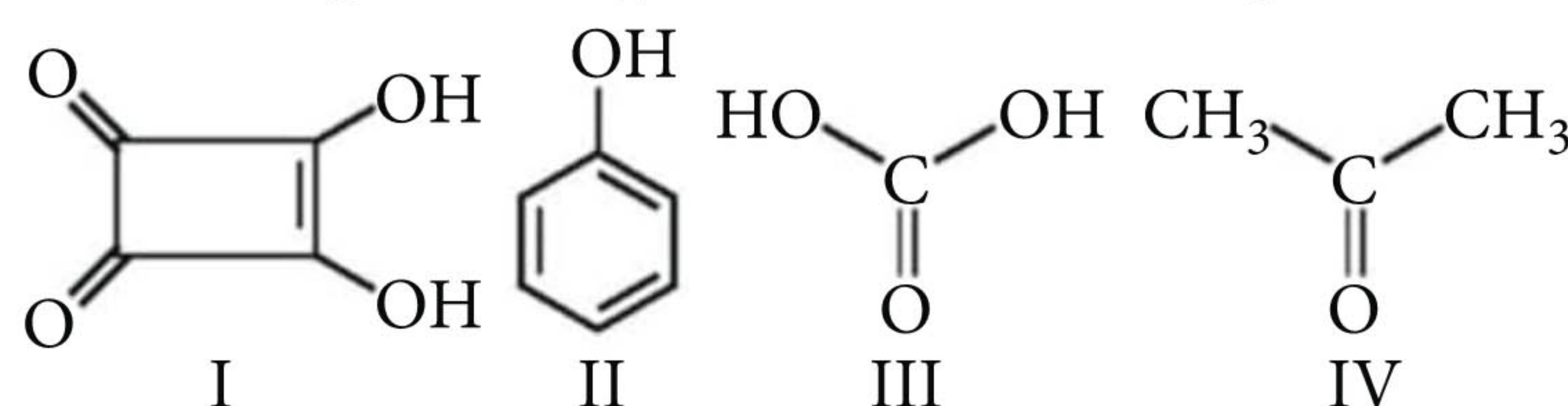
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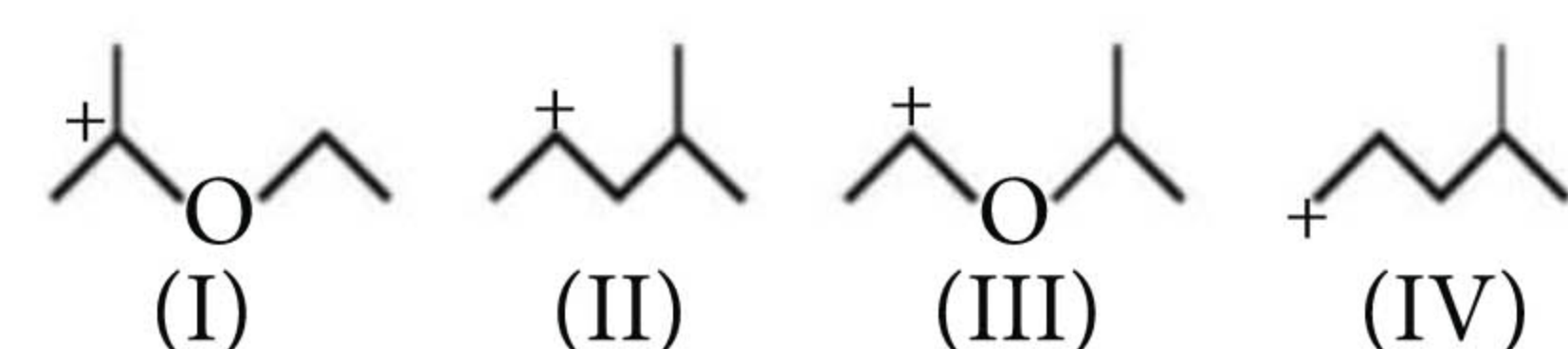
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7. For the given compounds, the acid strength order is



- (a) $I > IV > II > III$ (b) $III > I > II > IV$
 (c) $II > III > I > IV$ (d) $I > III > II > IV$
8. Which of the following statements is true for the given sequence of reactions?
 $B \xrightarrow{Z} X \xrightarrow{LiH} Y + LiBF_4$
 (a) Z is hydrogen.
 (b) Y is $LiBH_4$.
 (c) Z and Y are F_2 and B_2H_6 respectively.
 (d) Z is potassium hydroxide.

9. The correct stability order for the following species is



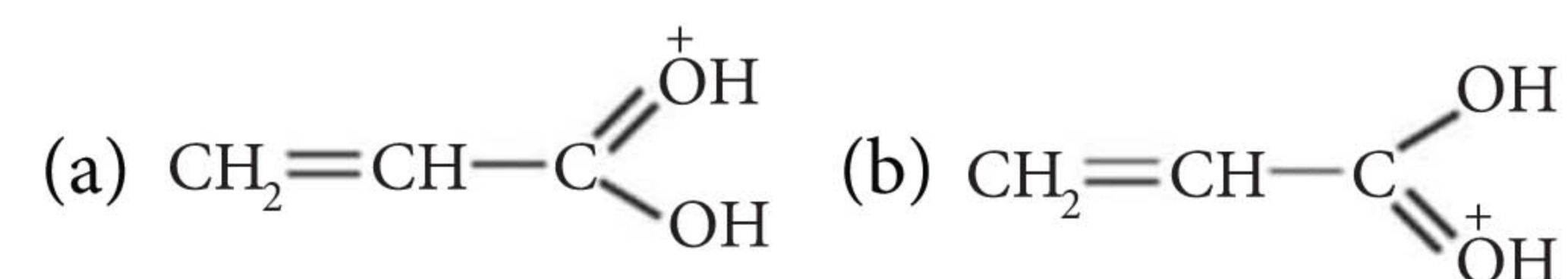
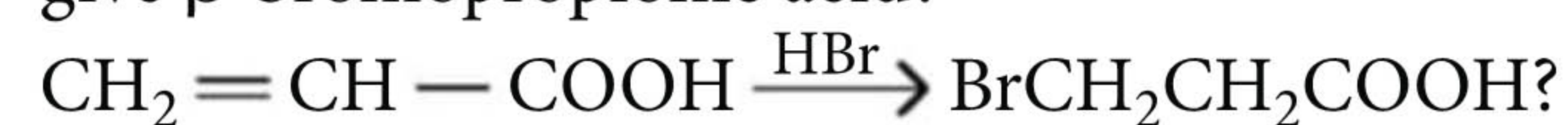
- (a) $(II) > (IV) > (I) > (III)$
 (b) $(I) > (II) > (III) > (IV)$
 (c) $(II) > (I) > (IV) > (III)$
 (d) $(I) > (III) > (II) > (IV)$
10. For which of the following parameters the functional isomers C_2H_5OH and CH_3OCH_3 would be expected to have the same values? (Assume ideal behaviour)
 (a) Heat of vaporisation
 (b) Vapour pressure at same temperature
 (c) Boiling point
 (d) Gaseous densities at same temperature and pressure.

More Than One Options Correct Type

11. Which of the following statements are correct with reference to Fe^{2+} and Fe^{3+} ions?
 (a) Fe^{3+} gives brown colour with ammonium thiocyanate.
 (b) Fe^{3+} gives brown colour with potassium ferrocyanide.
 (c) Fe^{3+} gives blue colour with potassium ferrocyanide.
 (d) Fe^{3+} gives brown colour with ammonium hydroxide.

12. Which of the following statements are correct?
 (a) Out of trimethylamine and trimethylphosphine, trimethylamine has higher dipole moment.
 (b) Out of $(SiH_3)_2O$ and $(CH_3)_2O$, $(SiH_3)_2O$ is more basic.
 (c) C-C bond length (in pm) in C_2 molecule is greater than O-O bond length in O_2 molecule.
 (d) $N(SiMe_3)_3$ and BF_3 molecules are isostructural.
13. Which of the following statements are correct about stability of chelates?
 (a) As the number of rings in the complex increases, stability of the complex (chelate) also increases.
 (b) A chelate having five membered rings is more stable if it contains double bonds.
 (c) A chelate having six membered rings is more stable if it does not contain double bonds.
 (d) Chelating ligands are at least bidentate ligands.

14. Which of the following intermediate species are formed in the reaction of acrylic acid with HBr to give β -bromopropionic acid?



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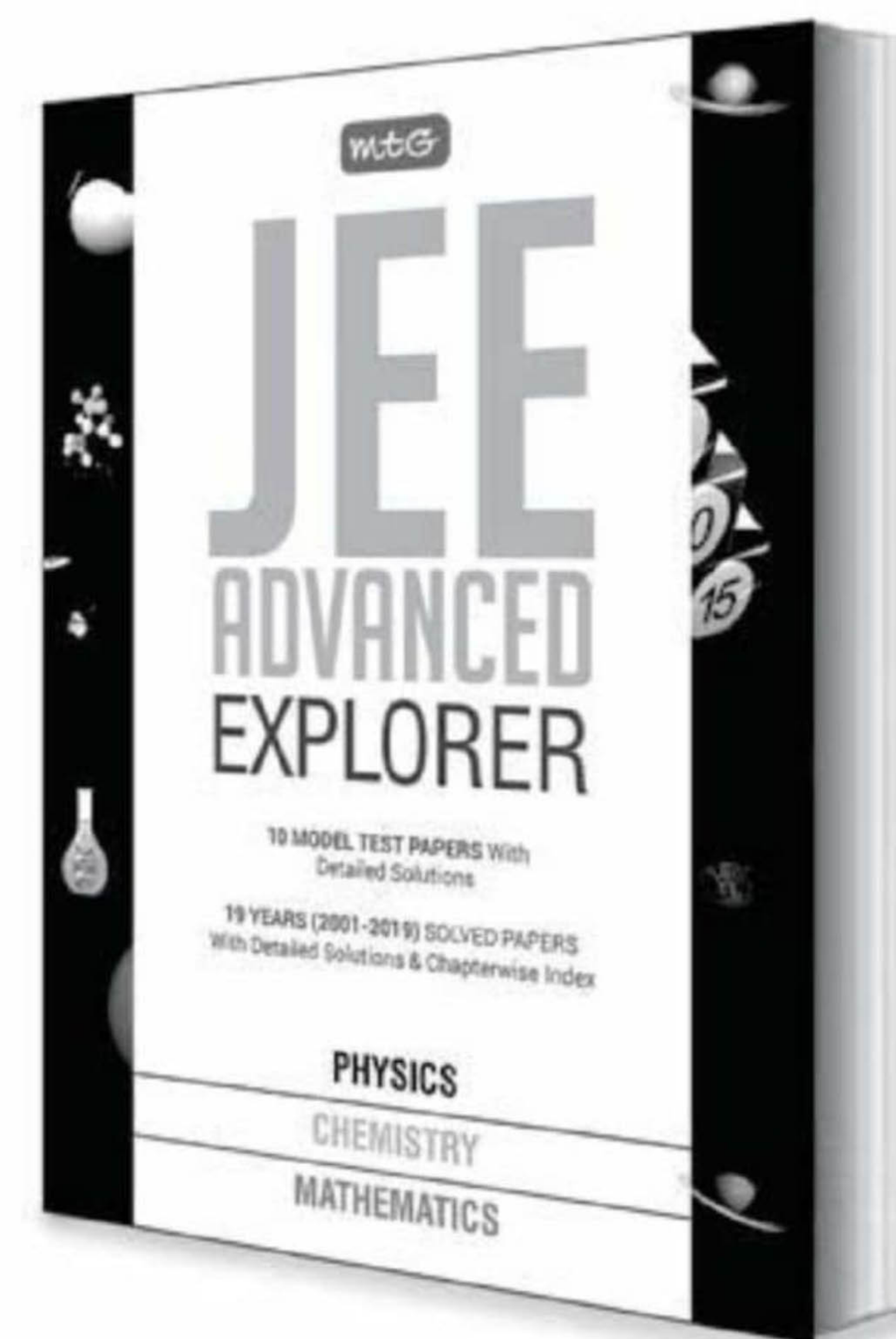
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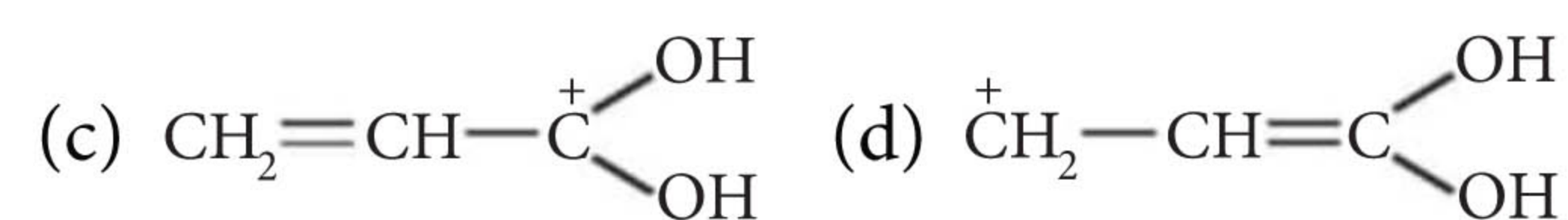
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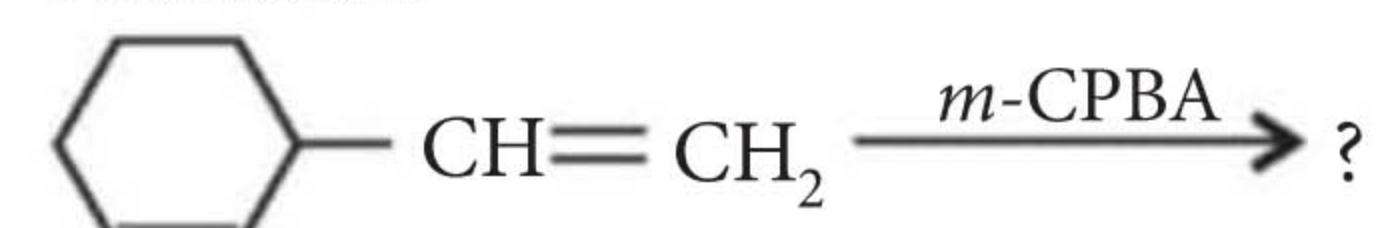
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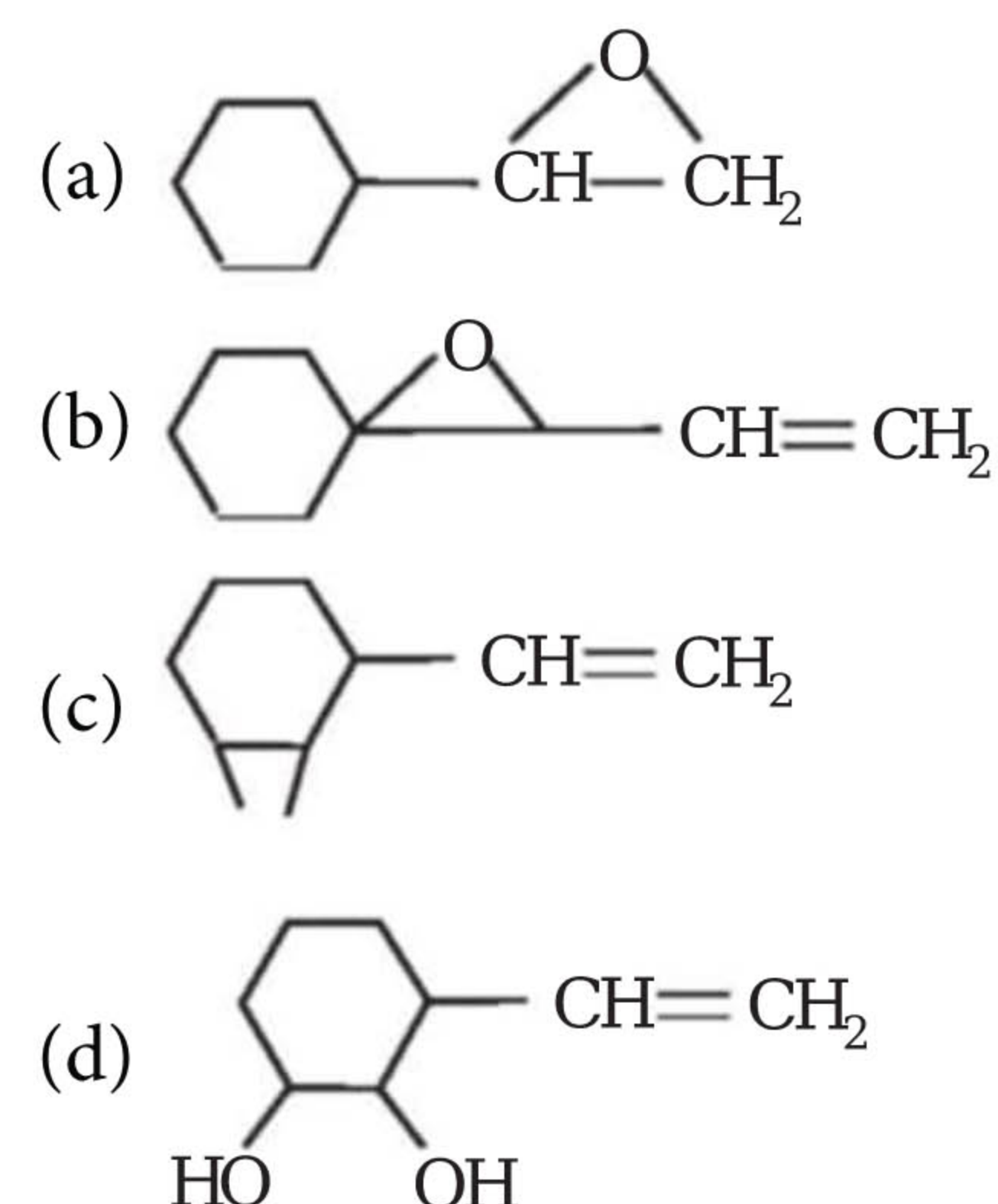
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15. Which of the following products are formed in the reaction?



(*m*-CPBA = *meta*-chloroperbenzoic acid)



SOLUTIONS

1. (d): Let W g of SO_2 and O_2 are taken

$$\text{Moles of } \text{SO}_2 = \frac{W}{64}; \text{ Moles of } \text{O}_2 = \frac{W}{32}$$

moles of $\text{O}_2 >$ moles of SO_2 , hence
 volume of O_2 at STP $>$ volume of SO_2 at STP.

$$\text{Molecules of } \text{O}_2 = \frac{WN_A}{32}; \text{ Molecules of } \text{SO}_2 = \frac{WN_A}{64}$$

Hence molecules of $\text{O}_2 >$ molecules of SO_2

$$\text{Number of atoms in } \text{O}_2 = \frac{WN_A}{32} \times 2 = \frac{WN_A}{16}$$

$$\text{Number of atoms in } \text{SO}_2 = \frac{WN_A}{64} \times 3 = \frac{3}{64} WN_A$$

$$\text{Ratio of atoms in } \text{SO}_2 : \text{O}_2 = \frac{3}{64} : \frac{1}{16} \text{ i.e., } 3 : 4$$

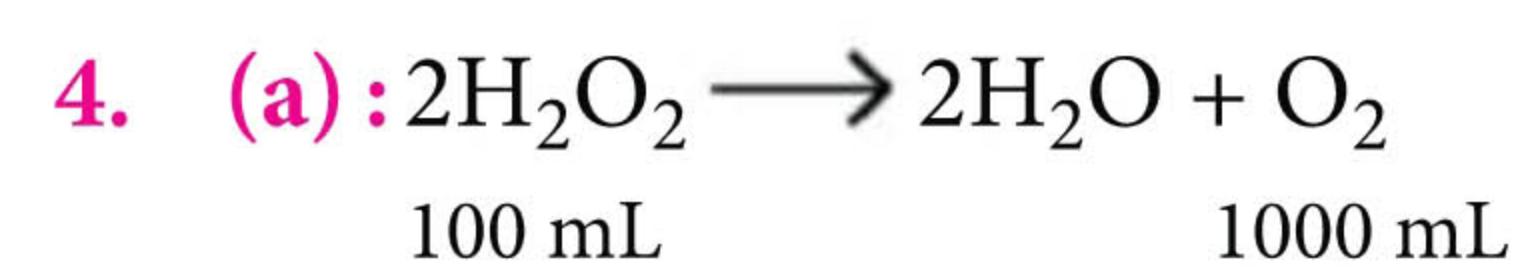
2. (b): Both O—H bonds in H_2O_2 do not lie in the same plane.

3. (d): $\Delta E_{2E \rightarrow E} = E - 2E = \frac{hc}{\lambda} \Rightarrow hc = -\lambda E$

$$\Delta E_{\frac{4E}{3} \rightarrow E} = E - \frac{4E}{3} = \frac{hc}{\lambda_1}$$

$$\Rightarrow \frac{-E}{3} = \frac{hc}{\lambda_1} \Rightarrow \lambda_1 = \frac{-hc \times 3}{E}$$

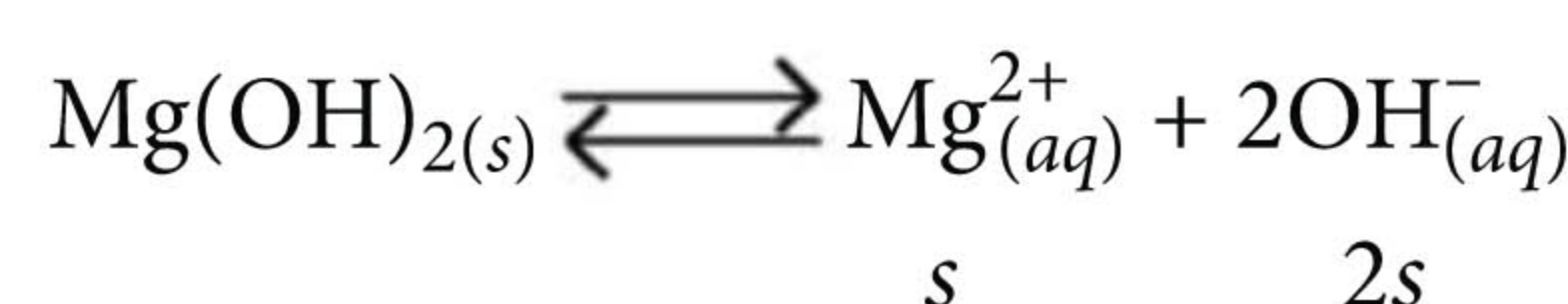
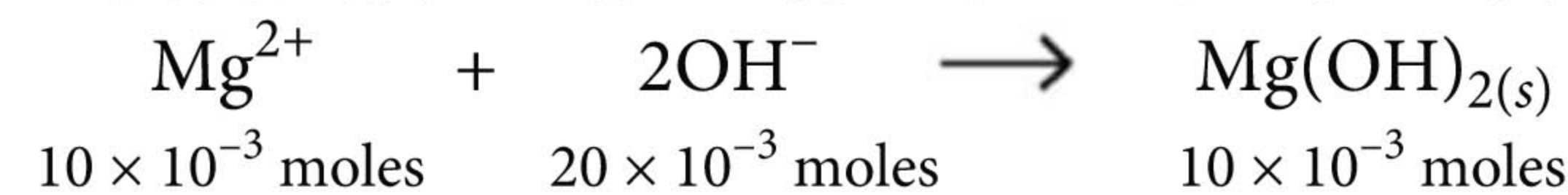
$$\lambda_1 = \frac{(-1) \times (-\lambda E)}{E} \times 3 = 3\lambda$$



or 1 mL of H_2O_2 will give 10 mL of O_2 at STP.
 Thus its volume strength is 10 volume.

5. (d): Moles of MgCl_2 solution = $0.1 \times 100 \times 10^{-3}$
 $= 10 \times 10^{-3}$ moles

moles of $\text{NaOH} = 0.2 \times 100 \times 10^{-3} = 20 \times 10^{-3}$ moles



Where, s is the solubility of $\text{Mg}(\text{OH})_2$ in the resulting solution.

$$K_{sp} = [\text{Mg}^{2+}] [\text{OH}^-]^2$$

$$= s \cdot (2s)^2$$

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$$K_{sp} = 4s^3 = 12 \times 10^{-12}$$

$$s = [3 \times 10^{-12}]^{1/3} = 1.44 \times 10^{-4} \text{ M}$$

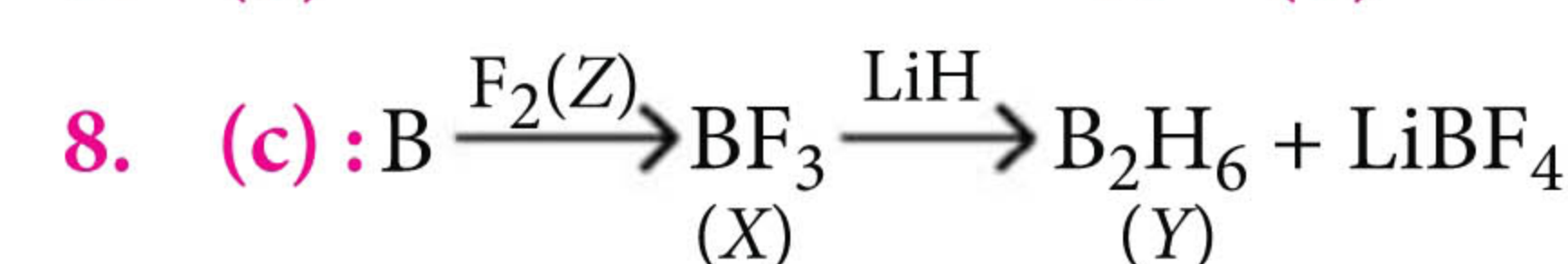
$$[\text{OH}^-] = 2s = 2.88 \times 10^{-4} \text{ M}$$

$$\text{or } \text{pOH} = 4 - \log 2.88 = 4 - 0.459 = 3.541$$

$$\therefore \text{pH} = 14 - \text{pOH} = 14 - 3.541 = 10.459$$

6. (b)

7. (d)



9. (d): (I) + *M* effect of 'O' and hyperconjugation effect of two- CH_3 groups.

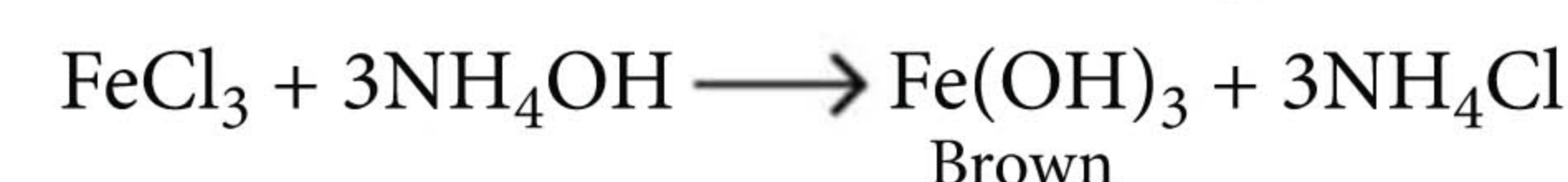
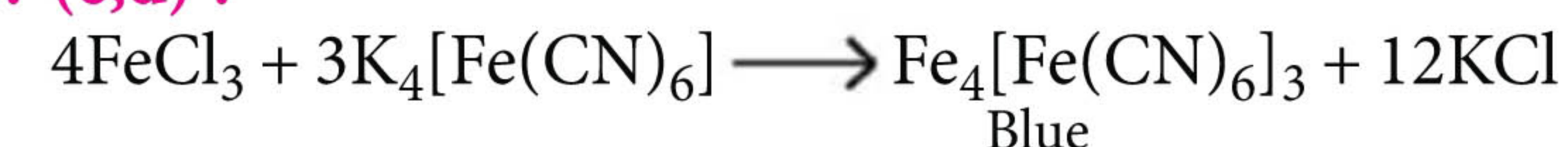
(II) is a simple 2° carbocation

(III) + *M* effect of 'O' and hyperconjugation effect of one- CH_3 groups.

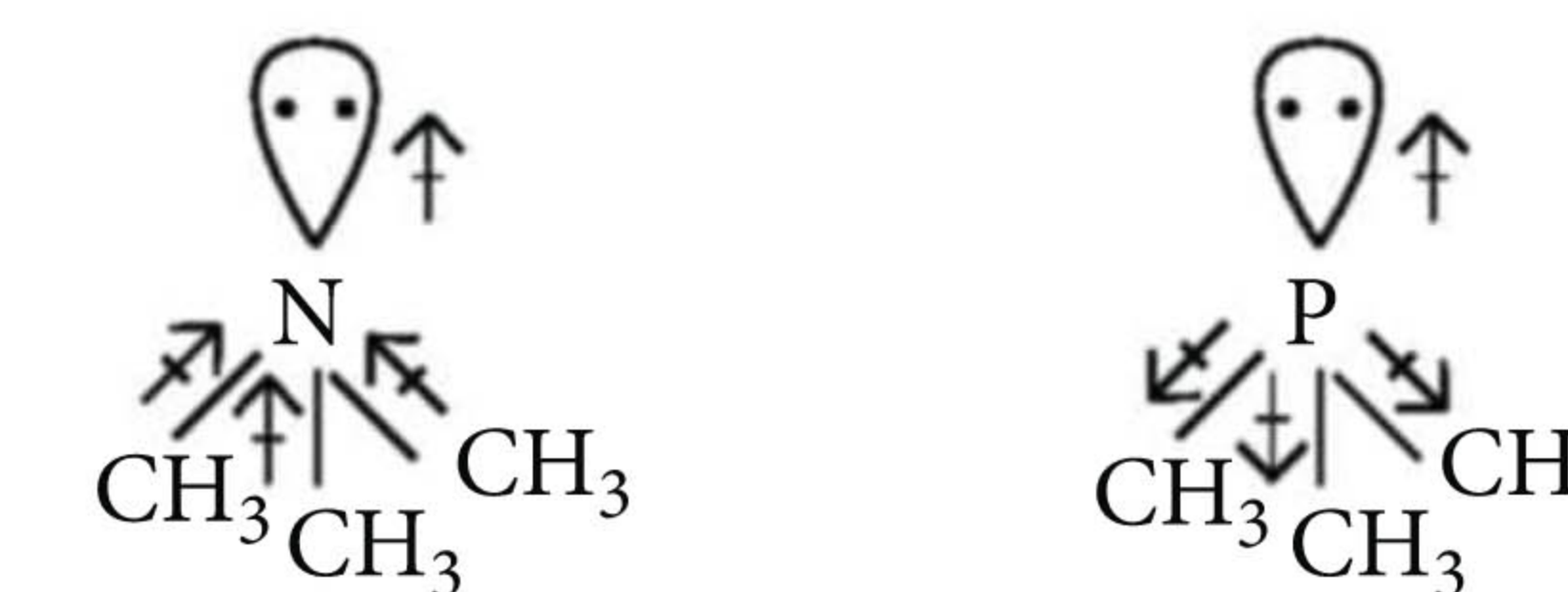
(IV) is a simple 1° carbocation.

10. (d): Except the gaseous densities all other parameters are different because of the presence of H-bonding in alcohol and the absence of the same in ether.

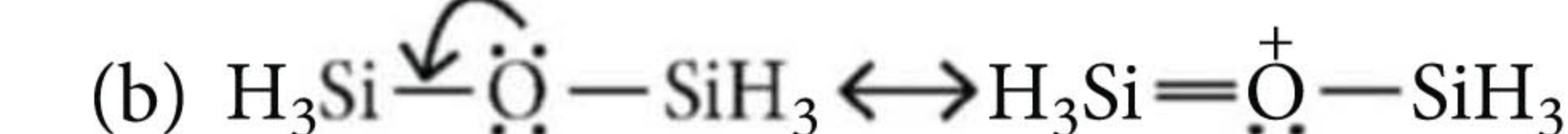
11. (c,d):



12. (a,c,d): (a) Nitrogen is more electronegative than phosphorus.



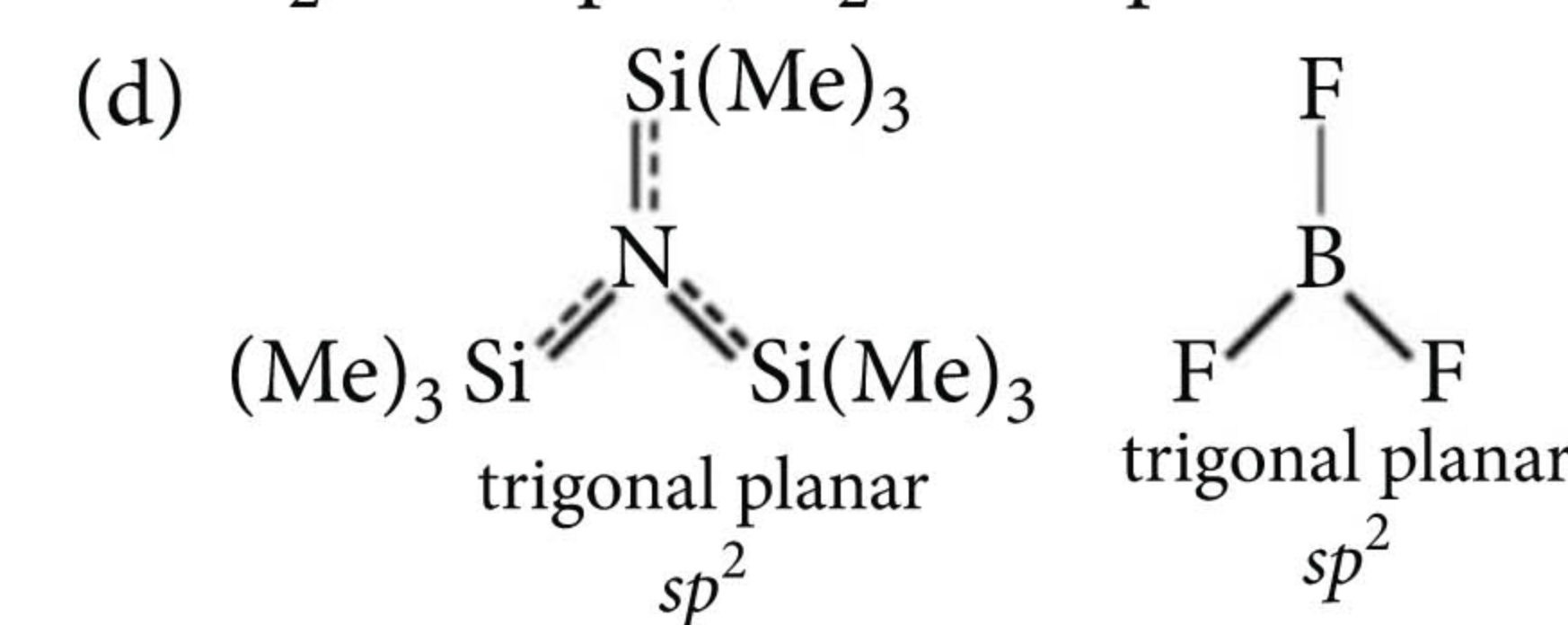
So, dipole moment of trimethylamine is greater than trimethylphosphine.



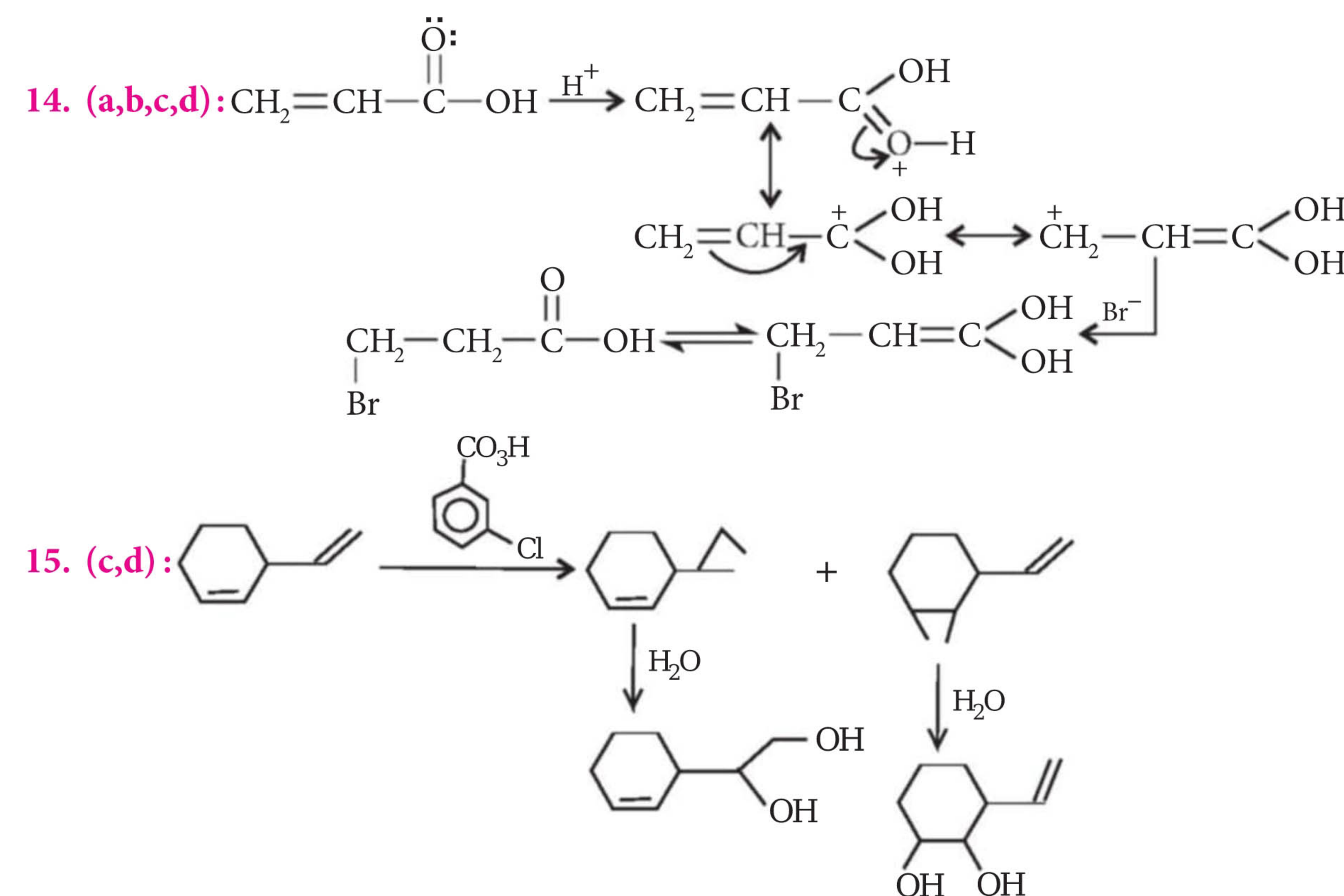
In trisilylether, the lone pair of electron on oxygen atom is less easily available for donation because of *pπ-dπ* delocalisation due to presence of the vacant *d*-orbital in Si. This however is not possible with carbon in $\text{CH}_3-\text{O}-\text{CH}_3$ due to the absence of *d*-orbital making it more basic.

(c) Bond order of C_2 and O_2 is same i.e., 2. In C_2 molecules both bonds are π -bonds whereas, there is one σ and one π -bond in O_2 molecule

$\text{C}_2 = 131 \text{ pm}$; $\text{O}_2 = 121 \text{ pm}$.



13. (a,d): Chelates of five-membered rings are more stable if they do not contain double bonds while the chelate of six-membered rings are more stable if they contain double bonds.



BRUSH UP for NEET/JEE CLASS-XI

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2020

Unit 3

States of Matter (Gaseous and Liquids) | Thermodynamics

States of Matter (Gaseous and Liquids)

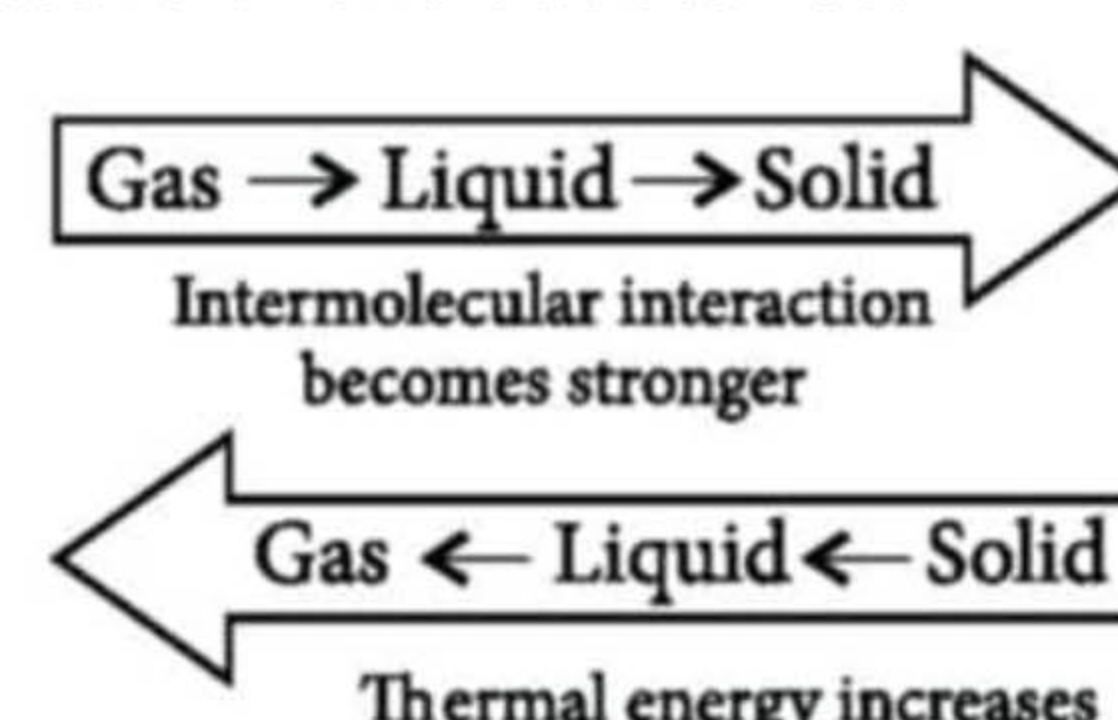
- Matter is typically found in one of the three different phases or states viz; solid, liquid or gas.
- The major factor that is responsible for the different behaviour of solids, liquids and gases is the nature of the interactions between the particles (atoms, ions or molecules) and the effect of thermal energy on the movement of the particles.

INTERMOLECULAR FORCES OF ATTRACTION

Types of Forces	Description
Dipole-induced dipole interaction	Forces between molecules having permanent dipole moment and molecule lacking permanent dipole moment.
Dipole-dipole interaction	Forces that exist between polar molecules where the positive end of one molecule attracts the negative end of another molecule.
London-dispersion forces	Forces that exist between molecules as a result of positive nuclei of one molecule attracting the electrons of another molecule.
Hydrogen bonding	Forces that exist between molecules that have a hydrogen atom bonded to a highly electronegative atom such as oxygen, nitrogen, or fluorine.

Intermolecular Forces vs Thermal Energy

- The energy which arises by motions of atoms or molecules of a body is known as thermal energy. It is the measure of average kinetic energy of the particles of matter and it is directly proportional to the temperature of the substance.



THE GAS LAWS

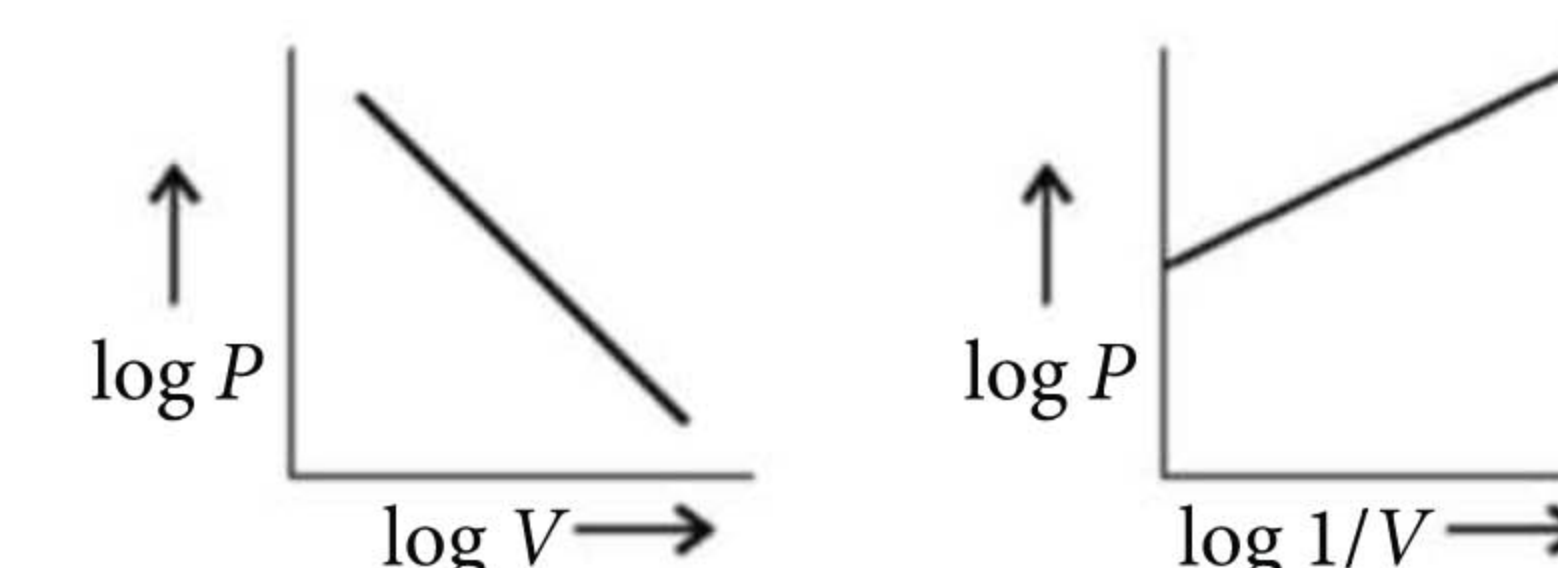
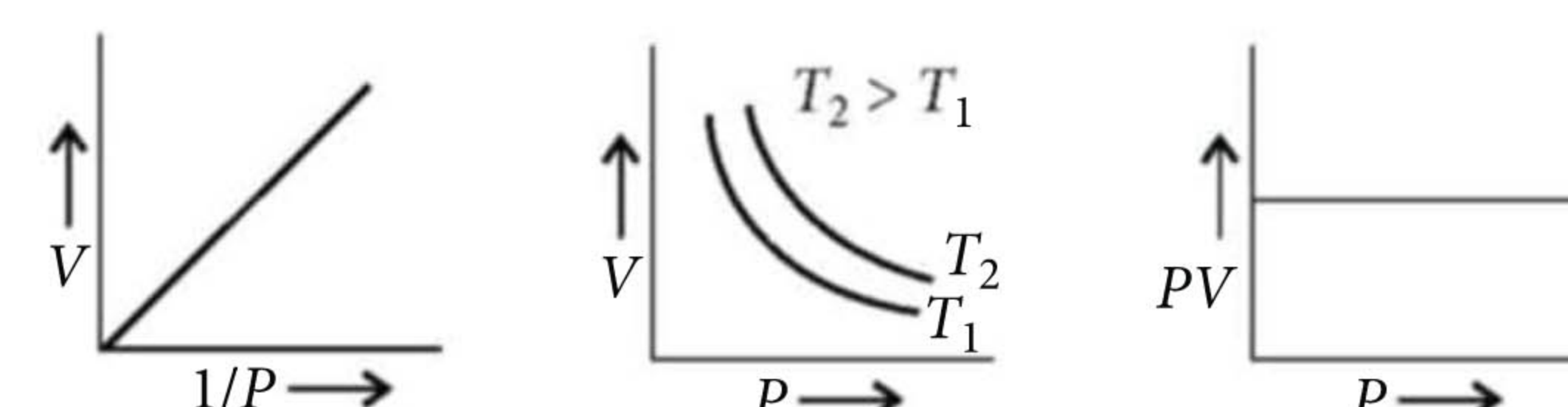
Boyle's Law

- At constant temperature, the pressure of a fixed amount of gas varies inversely with its volume.

$$P \propto \frac{1}{V} \quad (\text{at constant } T \text{ and } n)$$

$$\text{or } P_1 V_1 = P_2 V_2 = \text{constant}$$

- The plots drawn at constant temperature for a gas are called isotherms.

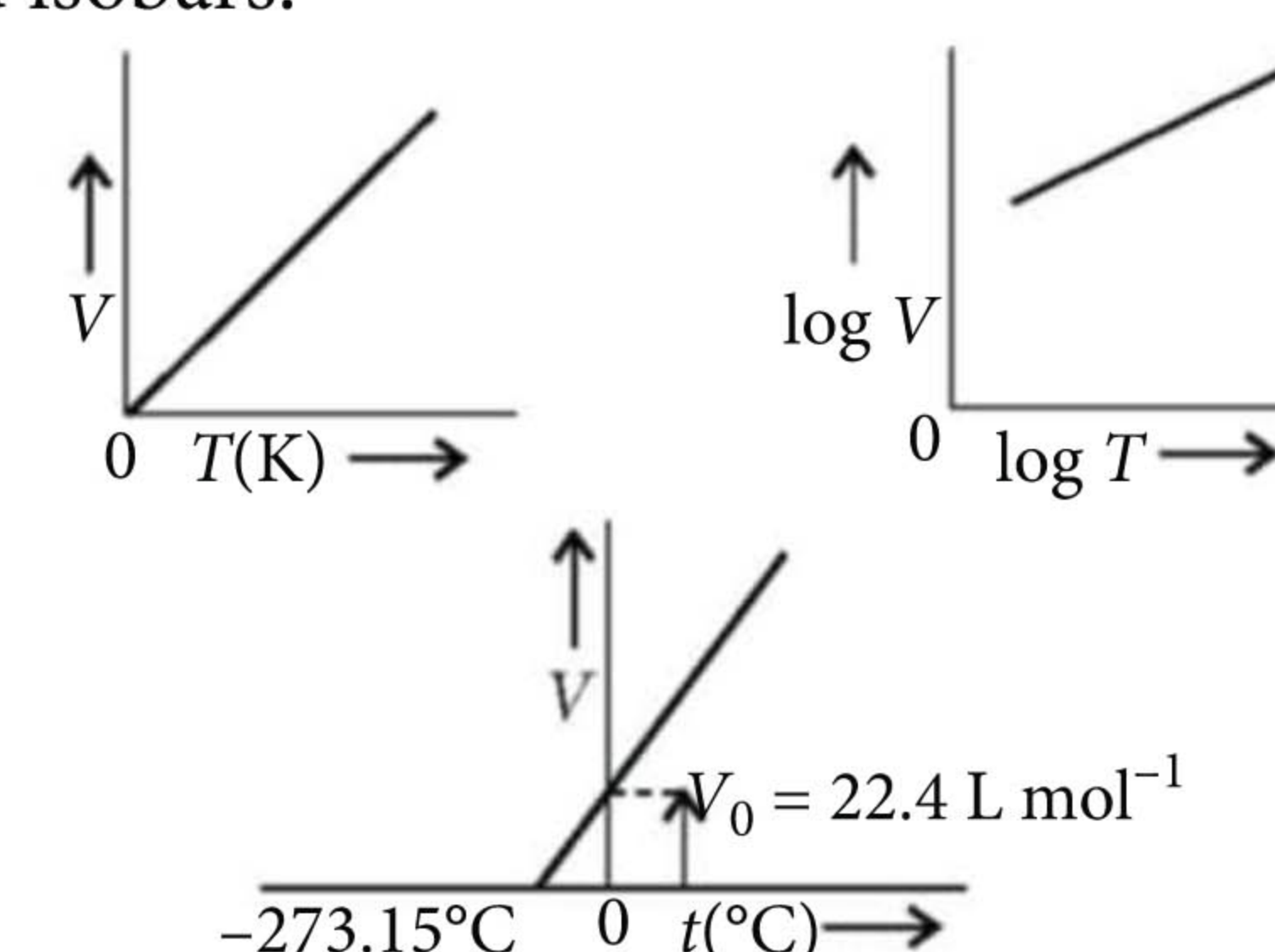


Charles' Law

- Pressure remaining constant, the volume of a fixed mass of a gas is directly proportional to its absolute temperature i.e., $V \propto T$

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \quad (\text{at constant } P)$$

- Graphs between V and T at constant pressure are called isobars.

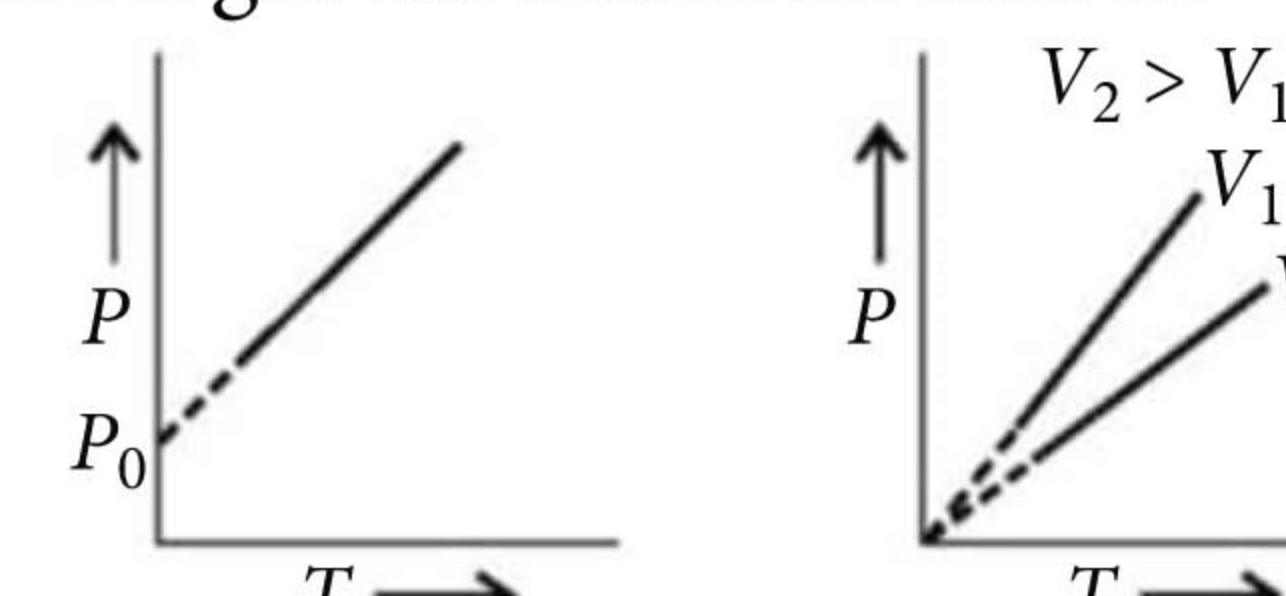


Gay-Lussac's Law or Amonton's Law

- At constant volume, pressure of a fixed amount of a gas varies directly with the temperature i.e., $P \propto V$

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \quad (\text{at constant } V)$$

- The plots drawn between P and T at constant volume for a gas are called isochores.



Avogadro's Law

- At constant, P and T , $V \propto n$.
or $n_1 V_1 = n_2 V_2$
At a given temperature and pressure equal volumes contain equal number of moles, independent of the kind of gas.

IDEAL GAS EQUATION

- Combined gas law: $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$
- Thus, $\frac{PV}{T} = \text{constant} = K$, $K \propto n$ or $K = nR$
 $PV/T = nR$ or $PV = nRT$

- The gases which obey the ideal gas equation under all conditions of temperature and pressure are called ideal gases.

Units of pressure	Units of volume	Values of gas constant (R)	Units of gas constant (R)
atm	L	0.0821	L atm K ⁻¹ mol ⁻¹
atm	cm ³	82.1	atm cm ³ K ⁻¹ mol ⁻¹
dynes cm ⁻²	cm ³	8.314×10^7	ergs K ⁻¹ mol ⁻¹
dynes cm ⁻²	cm ³	1.987	cal K ⁻¹ mol ⁻¹
Pa or N m ⁻²	m ³	8.314	J K ⁻¹ mol ⁻¹

- Relationship between molar mass and density:**
Let m be the mass of a gas in grams and M be the molar mass of that gas.

$$\text{We know, } n = \frac{m}{M}$$

$$\text{Now, } PV = nRT = \frac{m}{M} RT$$

$$P = \frac{m}{V} \frac{RT}{M} = \frac{dRT}{M} \quad \text{or} \quad M = \frac{dRT}{P}$$

$$\frac{dT}{P} = \frac{M}{R}, \text{ since } M \text{ and } R \text{ are constant for a gas.}$$

$$\therefore \frac{dT}{P} = \text{constant} \quad \therefore \frac{d_1 T_1}{P_1} = \frac{d_2 T_2}{P_2}$$

Dalton's Law of Partial Pressures

- The total pressure exerted by the mixture of non-reactive gases is equal to the sum of the partial pressures of individual gases.
- $P_{\text{total}} = p_1 + p_2 + p_3 + \dots$
 $p_1 = P_{\text{total}} \times \text{mole fraction of gas 1.}$
i.e., partial pressure = total pressure \times mole fraction

Graham's Law of Diffusion

- Under similar conditions of temperature and pressure, rates of diffusion of different gases are inversely proportional to the square root of their densities.

$$\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}} \quad \text{or} \quad \frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$$

PEEP INTO PREVIOUS YEARS

- The volume occupied by 1.8 g of water vapour at 374°C and 1 bar pressure will be [Use $R = 0.083 \text{ bar L K}^{-1} \text{ mol}^{-1}$]
(a) 96.66 L (b) 55.87 L (c) 3.10 L (d) 5.37 L
(Odisha NEET 2019)

2. At 300 K, the density of a certain gaseous molecule at 2 bar is double to that of dinitrogen (N_2) at 4 bar. The molar mass of gaseous molecule is
 (a) 56 g mol^{-1} (b) 112 g mol^{-1}
 (c) 224 g mol^{-1} (d) 28 g mol^{-1}

(JEE Main 2017)

3. Equal moles of hydrogen and oxygen gases are placed in a container with a pin-hole through which both can escape. What fraction of the oxygen escapes in the time required for one-half of the hydrogen to escape?
 (a) $3/8$ (b) $1/2$
 (c) $1/8$ (d) $1/4$ (NEET 2016)

KINETIC GAS EQUATION

$$PV = \frac{1}{3} mnu^2$$

where, P = pressure of gas

V = volume of gas

m = mass of one molecule of gas

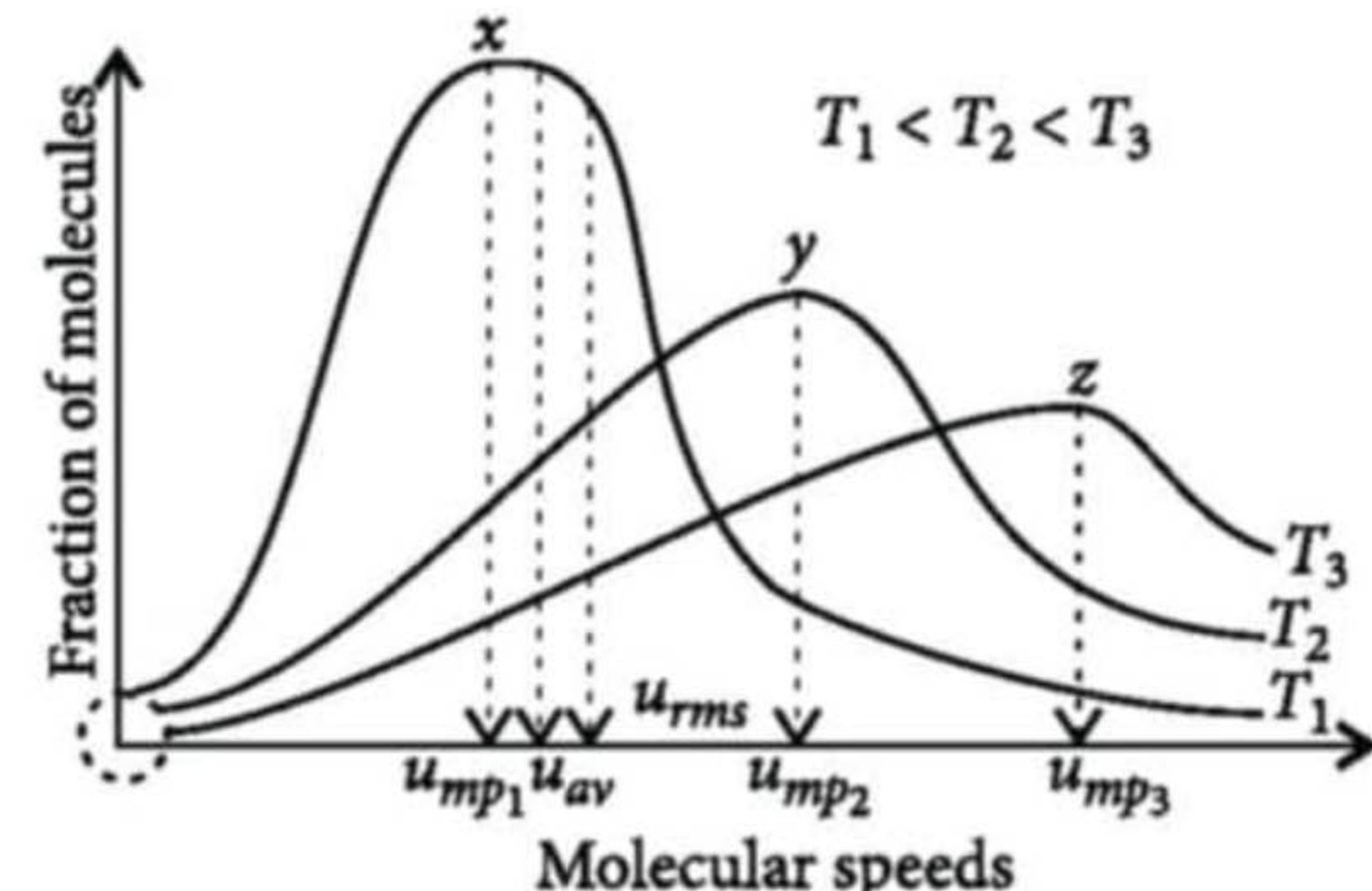
n = number of molecules of gas

u = root mean square speed of molecules

Kinetic Energy and Molecular Speeds

Average speed	Root mean square speed	Most probable speed
$u_{av} = \sqrt{\frac{8RT}{\pi M}}$	$u_{rms} = \sqrt{\frac{3RT}{M}}$	$u_{mp} = \sqrt{\frac{2RT}{M}}$

Maxwell's Distribution of Speeds



Signifies that speed is never zero but it tends towards zero

- Average kinetic energy per molecule

$$= \frac{3}{2} \cdot \frac{R}{N} \cdot T = \frac{3}{2} kT$$
 where, k = Boltzmann constant
 $= 1.3806 \times 10^{-16} \text{ erg deg}^{-1}$
- Total kinetic energy of n moles of a gas $= n \times \frac{3}{2} RT$.

$$\begin{aligned} \text{Most probable : average : r.m.s.} &= \sqrt{2} : \sqrt{\frac{8}{\pi}} : \sqrt{3} \\ &= 1:1.128:1.224 \end{aligned}$$

$$u_{rms} > u_{av} > u_{mp}$$

Kinetic Molecular Theory of Gases

- The gas laws were based on simple experimental facts hence, a theoretical proof or derivation for the same was proposed, on the basis of kinetic molecular theory of gases, by Maxwell and Boltzmann as :
 - Gases are made up of a large number of small molecules whose size is negligible as compared to the distance of separation between them.
 - Molecules move randomly in different directions with different speeds.
 - The intermolecular forces of attraction or repulsion are almost negligible, except when molecules collide.
 - The collisions are called elastic collisions because no energy change occurs when two molecules collide, i.e., the total kinetic energy remains constant.
 - The average kinetic energy of a molecule is proportional to its absolute temperature.
 - The pressure exerted by the gas is due to bombardment of its molecules on the walls of the container per unit area.

REAL GASES

- The gases which obey the gas laws only at low pressure and high temperature are called real gases.

van der Waals' Equation of State

The deviations from ideal gas behaviour can be ascertained to the following faulty assumptions by kinetic theory of gases :

- The real volume of the gas molecules is negligible when compared to the volume of the gas.
- There are no forces of attraction or repulsion between the gas molecules. Hence, van der Waals suggested the following corrections :
 - The gas molecules possess finite volume and hence should not be neglected. It is especially true at high pressures and low temperatures and should be accounted for.
 - In case of real gases, both the forces of attraction as well as repulsion operate between gas molecules.
 - The ideal gas equation can be written after volume correction as :
 $P(V - nb) = nRT$

- After pressure correction :

$$P_{\text{ideal}} = P_{\text{real}} + a \left(\frac{n^2}{V^2} \right)$$

$$\left(P + \frac{an^2}{V^2} \right) (V - nb) = nRT$$

a, b are van der Waals' constants; different for each gas.

Unit of $a \rightarrow \text{atm L}^2 \text{ mol}^{-2}$; S.I. unit $\rightarrow \text{Pa m}^6 \text{ mol}^{-2}$

Unit of $b \rightarrow \text{L mol}^{-1}$; S.I. unit $\rightarrow \text{m}^3 \text{ mol}^{-1}$

- Significance of van der Waals constants.** ' a ' is a measure of the magnitude of attractive forces whereas ' b ' is a measure of the effective size of the gas molecules. $b = 4v$ where v is actual volume of gas molecules. ' b ' is called excluded volume or co-volume. Greater the value of ' a ' more easily the gas is liquefiable.

- Compressibility factor (Z) :** It measures the deviation from ideal behaviour and is given as

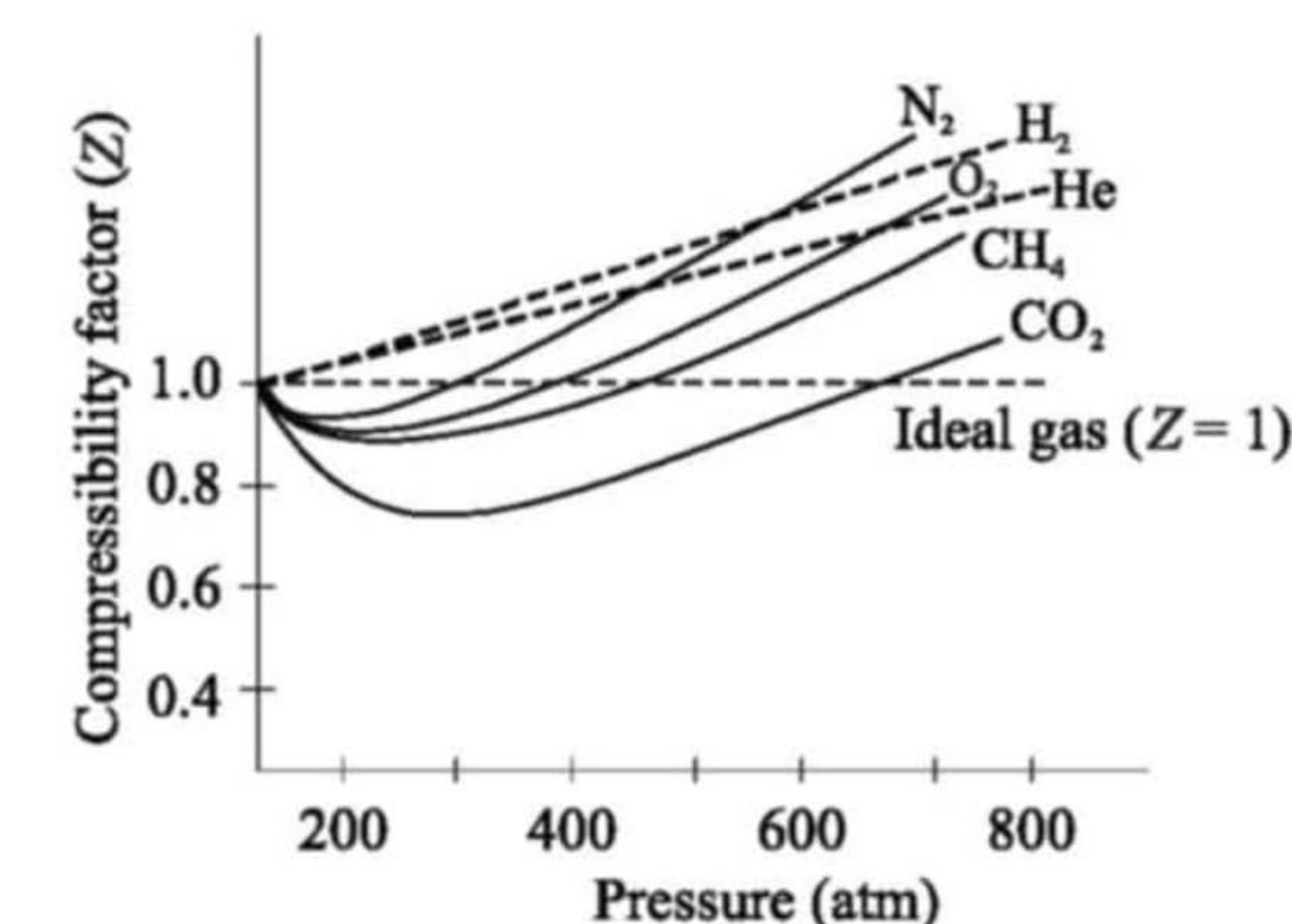
$$Z = \frac{PV}{nRT}; Z = 1 \text{ for ideal gas, } Z \neq 1 \text{ for real gases,}$$

$$Z = \frac{V_{\text{real}}}{V_{\text{ideal}}}$$

$Z > 1$ for positive deviation from ideal behaviour,

$Z < 1$ for negative deviation from ideal behaviour.

- The isotherms for one mole of different gases, plotted against the Z value and pressure, P at 0°C are shown as :



- For gases like He, H_2 the Z value increases with increase in pressure (positive deviation). It is because, the repulsive forces become more significant and the attractive forces become less dominant. Hence, these gases are difficult to condense.
- For gases like CH_4, CO_2, NH_3 , etc., the Z value decreases initially (negative deviation) but increases

at higher pressure. It is because at low pressures, the attractive forces are more dominant over the repulsive forces, whereas at higher pressures the repulsive forces become significant as the molecules approach closer to each other.

- But for all the gases, the Z value approaches one at very low pressures, indicating the ideal behaviour.
- Boyle temperature (or Boyle point)** is the temperature at which a real gas obeys ideal gas law over an appreciable range of pressure.
- Critical temperature (T_c)** is the temperature above which a gas cannot be liquefied howsoever high pressure may be applied on the gas. The corresponding pressure and volume are called critical pressure (P_c) and critical volume (V_c).

LIQUID STATE

- Liquid state is intermediate between gaseous and solid states. They possess fluidity like gases but incompressibility like solids.

Properties	Description
Surface tension	Force per unit length acting perpendicular to the tangential line on the surface. It decreases with increases in temperature. $r = \frac{\text{work (w)}}{\text{change in area (A)}} = \frac{\text{Force (F)}}{\text{length (l)}}$ cgs unit = dynes cm^{-1} SI unit = Nm^{-1}
Viscosity	Internal resistance of flow in liquids which one layer offers to another layer trying to pass over. $\text{coefficient of viscosity, } \eta = \frac{f \cdot dx}{A \cdot dv}$ SI unit of viscosity coefficient = N sec m^{-2} cgs unit of viscosity coefficient = poise
Vapour pressure	It is the pressure exerted by the vapours on the liquid surface. It increases with rise in temperature. $\log \frac{P_2}{P_1} = \frac{\Delta H_{\text{vap}}}{2.303R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$ Increases with increase in temperature due to decrease in the magnitude of interparticle forces.

PEEP INTO PREVIOUS YEARS

4. A gas at 350 K and 15 bar has molar volume 20 percent smaller than that for an ideal gas under the same conditions. The correct option about the gas and its compressibility factor (Z) is
 (a) $Z < 1$ and repulsive forces are dominant
 (b) $Z > 1$ and attractive forces are dominant
 (c) $Z > 1$ and repulsive forces are dominant
 (d) $Z < 1$ and attractive forces are dominant.
 (NEET 2019)
5. Which of the following statement(s) is (are) correct regarding the root mean square speed (u_{rms}) and average translational kinetic energy (E_{av}) of a molecule in a gas at equilibrium?
 (a) u_{rms} is inversely proportional to the square root of its molecular mass.
 (b) E_{av} is doubled when its temperature is increased four times.
 (c) u_{rms} is doubled when its temperature is increased four times.
 (d) E_{av} at a given temperature does not depend on its molecular mass. (JEE Advanced 2019)
6. A liquid can exist only
 (a) between triple point and critical point
 (b) at any temperature above melting point
 (c) between melting point and critical point
 (d) between boiling and melting points.
 (Karnataka CET 2016)

POINTS FOR EXTRA SCORING

- Normal boiling point of a liquid is approximately 2/3 of its critical temperature.
- T_i (inversion temperature) = $\frac{2a}{R \cdot b}$
- Average K.E. = $\bar{E}_k = \frac{3}{2} kT$
- Critical constants : $V_c = 3b$, $T_c = \frac{8a}{27Rb}$,
 $P_c = \frac{a}{27b^2}$, $P_c V_c = \frac{3}{8} kT_c$
- Volume coefficient (α_V) = $\frac{V_t - V_0}{V_0 \times t}$

- Pressure coefficient (α_p) = $\frac{P_t - P_0}{P_0 \times t}$
- $\frac{\Delta H_{\text{vap}}}{T_b} = 88 \text{ J K}^{-1} \text{ mol}^{-1}$ (Trouton's rule)
- A number of substances are known which when added to water, lower its surface tension. These substances are called surfactants or surface active agents e.g. CH_3OH , $\text{C}_2\text{H}_5\text{OH}$, soaps, etc.
- Surface tension decreases with increase in temperature and becomes zero at the critical temperature while viscosity of a liquid decreases with increase in temperature by about 2% per degree rise in temperature.

Thermodynamics

- The study of the flow of heat or any other form of energy in or out of a system as it undergoes a physical or chemical transformation is called thermodynamics.
- **System** : The specified portion of the universe under observation.
- **Surrounding** : The remaining part of the universe which is not a part of the system and is not under study.

TYPES OF SYSTEM

- **Open system** : can exchange matter as well as energy with surroundings.
- **Closed system** : can exchange energy but not matter with surroundings.

- **Isolated system** : cannot exchange matter as well as energy with surroundings.

THERMODYNAMIC PROPERTIES

- **Intensive properties** : Properties which do not depend on the amount of matter present in the system.
 Examples : Pressure, Temperature, Density, Melting point, Boiling point etc.
- **Extensive properties** : Properties which depend on the amount of matter present in the system.
 Examples : Mass, Volume, Heat capacity, Enthalpy, Entropy etc.
 Ratio of two extensive properties is always intensive,
 i.e., $\frac{\text{Extensive}}{\text{Extensive}} = \text{Intensive}$

$$\text{e.g., } \frac{\text{Mass}}{\text{Volume}} = \text{Density}$$

THERMODYNAMIC PROCESSES

- **Isothermal** : Temperature remains constant throughout the process i.e., $dT = 0$
- **Isobaric** : Pressure remains constant throughout the process i.e., $dP = 0$
- **Isochoric** : Volume remains constant throughout the process i.e., $dV = 0$
- **Adiabatic** : System does not exchange heat with surrounding i.e., $dq = 0$
- **Cyclic Process** : System undergoes a number of different processes and finally returns to its initial state.

Reversible Process (Quasi-static) and Irreversible Process

- A process which is carried out so slowly that the system and the surroundings are nearly in equilibrium is known as a reversible process. If this condition does not hold good, the process is said to be, irreversible.
- In a reversible process the driving force is infinitesimally larger than the opposing force. If the driving force is made infinitely smaller than opposing force, the system can be brought back without producing any permanent change.
- All natural processes are irreversible process.
- **Spontaneous process** : Proceeds on its own i.e., without any external help.

FIRST LAW OF THERMODYNAMICS

- It is a law of conservation of energy which states that energy can neither be created nor destroyed, although it can be converted from one form to another.
 Mathematically : ΔE or $\Delta U = q + W$ or $q = \Delta U - W$
- **Internal Energy (U)** : It is the total energy within a system which is the sum of all types of energies (chemical, electrical, mechanical or any other type) of the system and is a state function.
- **Sign convention for q and w** :
 – If work is done on the system, W is positive.
 – If work is done by the system, W is negative.
 – If heat is absorbed by the system, q is positive.
 – If heat is given out by the system, q is negative.

Applications

- **Isothermal reversible expansion of an ideal gas** :
 – The overall work done in an isothermal reversible expansion of the ideal gas

$$\therefore w = -nRT \ln \frac{P_1}{P_2} = -2.303nRT \log \frac{P_1}{P_2}$$
 – The work done during an isothermal reversible compression can be given as :

$$w = 2.303nRT \log \frac{P_1}{P_2}$$
 Thus, work done in isothermal compression has exactly the same value with positive sign.
- **Free expansion** : Expansion of a gas in vacuum ($P_{\text{ex}} = 0$) is called free expansion. No work is done during free expansion of an ideal gas whether the process is reversible or irreversible.
 i.e., $\Delta U = q - P_{\text{ex}} \Delta V$
 At constant V , $\Delta U = q_V$
- **Isothermal and free expansion of an ideal gas** :
 – For isothermal expansion of an ideal gas into vacuum; $w = 0$ since, $P_{\text{ex}} = 0$
 – For isothermal irreversible change;
 $q = -w = P_{\text{ex}}(V_f - V_i)$
 – For isothermal reversible change;

$$q = -w = 2.303 nRT \log \frac{V_f}{V_i}$$
 – For adiabatic change; $q = 0$, $\Delta U = w_{\text{ad}}$

ENTHALPY (H)

- Total heat content of the system at constant pressure is known as its enthalpy.
 – Its absolute value can not be determined.
 – Mathematically, it is given as

$$\Delta H = \Delta U + P \Delta V$$
- For exothermic reaction (i.e., heat released during the reaction) ΔH is negative i.e., $\Delta H < 0$. Whereas for endothermic reaction (i.e., heat absorbed during the reaction), ΔH is positive i.e., $\Delta H > 0$.
 Enthalpy change at constant pressure (q_p) = ΔH
 Enthalpy change at constant volume (q_v) = ΔU

$$q_p = q_v + P \Delta V \text{ or } q_p = q_v + \Delta n_g RT$$
 where Δn_g = Difference in the number of moles of gaseous product and gaseous reactant.
- **Heat capacity (C)** of a system is the amount of heat required to raise the temperature of the system through 1 °C.

$$C = \frac{q}{\Delta T} \text{ or } q = C \Delta T$$

- **Specific heat capacity or specific heat (c)** of a substance is the amount of heat required to raise the temperature of 1 g of the substance through 1 °C.
 $q = mc\Delta T$

– Specific heat capacity of water = 1 cal g⁻¹ K⁻¹ or 4.18 J g⁻¹ K⁻¹

- **Relation between C_p and C_v for an ideal gas :**

$$C_p = \frac{\Delta H}{\Delta T}, C_v = \frac{\Delta U}{\Delta T}$$

$$C_p - C_v = R, C_p/C_v = \gamma$$

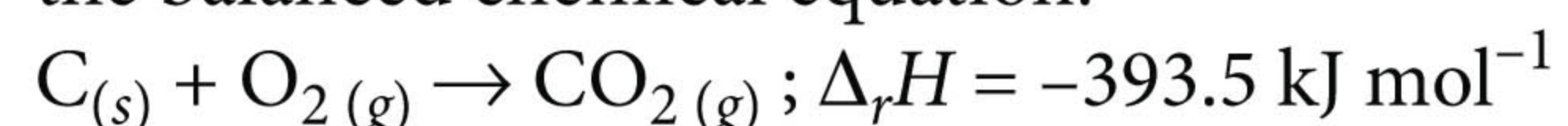
For monoatomic gas, $\gamma = 1.66$; for diatomic gas, $\gamma = 1.40$; for triatomic gas, $\gamma = 1.33$.

- **Measurement of ΔU :** It is done in bomb calorimeter.

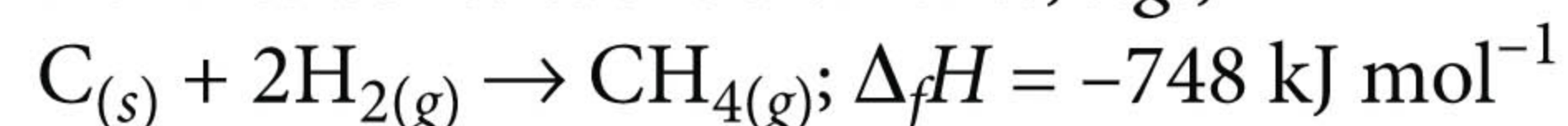
$$\Delta U = C \times \Delta t \times \frac{M}{m}; \text{ where, } m \text{ is mass of substance}$$

taken, M is its molar mass, C is the heat capacity of the calorimeter and Δt is the rise in temperature.

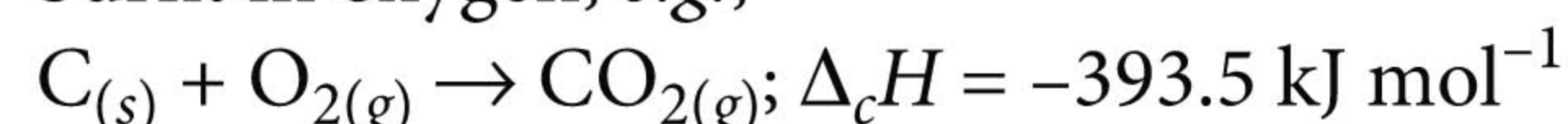
- **Enthalpy of reaction :** It is defined as the change in enthalpy, or the amount of heat evolved or absorbed when the number of moles of reactants reacts completely to give the products as given by the balanced chemical equation.



- **Enthalpy of formation :** It is the change in enthalpy when one mole of a substance is formed directly from its constituent elements, e.g.,

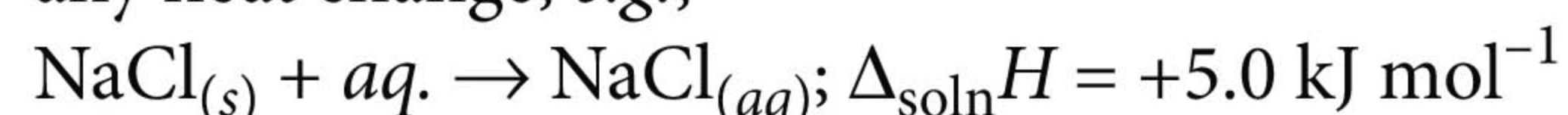


- **Enthalpy of combustion :** It is the change in enthalpy when one mole of a substance is completely burnt in oxygen, e.g.,

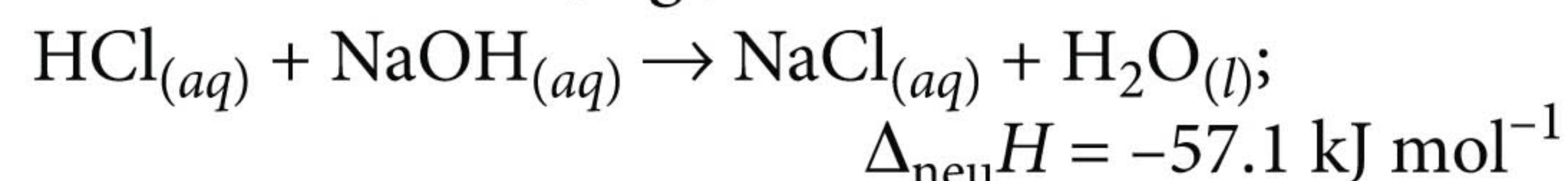


$\Delta_c H$ is always negative as heat is always evolved during combustion.

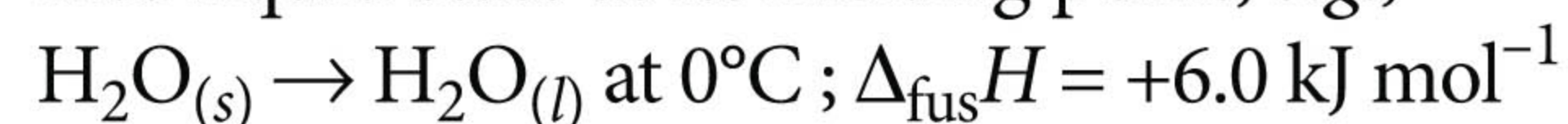
- **Enthalpy of solution :** It is the change in enthalpy when one mole of a substance is dissolved in excess of water so that further dilution does not involve any heat change, e.g.,



- **Enthalpy of neutralisation :** It is the change in enthalpy when one gram equivalent of an acid is completely neutralised by 1 g equivalent of a base in dilute solutions, e.g.,



- **Enthalpy of fusion :** It is the change in enthalpy when one mole of a solid is completely converted into liquid state at its melting point, e.g.,

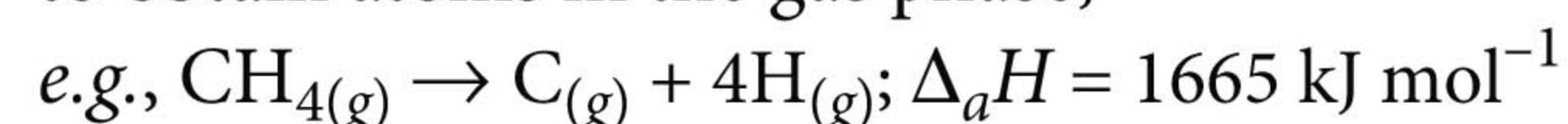


- **Enthalpy of vapourisation :** It is the change in enthalpy when one mole of a liquid is completely converted into its vapours at its boiling point, e.g.,
 $H_2O_{(l)} \rightarrow H_2O_{(g)} \text{ at } 373 \text{ K}; \Delta_{vap} H = +40.6 \text{ kJ mol}^{-1}$

- **Enthalpy of sublimation :** It is the change in enthalpy when one mole of a solid is directly converted into vapours.

$$\text{Also, } \Delta_{sub} H = \Delta_{fus} H + \Delta_{vap} H$$

- **Enthalpy of atomization :** It is the change in enthalpy on breaking one mole of bonds completely to obtain atoms in the gas phase,



- **Bond enthalpy :** It is the change in enthalpy associated with breaking and making of chemical bonds, e.g.,



- **Hess's law of constant heat summation :** If a reaction takes place in several steps then its standard reaction enthalpy is the sum of the standard enthalpies of the intermediate reactions into which the overall reaction may be divided at the same temperature.

$$\Delta_r H = \Delta_r H_1 + \Delta_r H_2 + \Delta_r H_3 \dots$$

✓ PEEP INTO PREVIOUS YEARS

7. An ideal gas expands isothermally from 10⁻³ m³ to 10⁻² m³ at 300 K against a constant pressure of 10⁵ N m⁻². The work done on the gas is

(a) +270 kJ (b) -900 J

(c) +900 kJ (d) -900 kJ

(Odisha NEET 2019)

8. The enthalpy change on freezing of 1 mol of water at 5°C to ice at -5°C is

(Given : $\Delta_{fus} H = 6 \text{ kJ mol}^{-1}$ at 0°C,

$C_p(H_2O, l) = 75.3 \text{ J mol}^{-1} \text{ K}^{-1}$,

$C_p(H_2O, s) = 36.8 \text{ J mol}^{-1} \text{ K}^{-1}$)

(a) 5.81 kJ mol⁻¹ (b) 6.56 kJ mol⁻¹

(c) 6.00 kJ mol⁻¹ (d) 5.44 kJ mol⁻¹

(JEE Main 2017)

9. A gas is allowed to expand in a well insulated container against a constant external pressure of 2.5 atm from an initial volume of 2.50 L to a final volume of 4.50 L. The change in internal energy ΔU of the gas in joules will be

(a) -500 J

(b) -505 J

(c) +505 J

(d) 1136.25 J

(NEET 2017)

SECOND LAW OF THERMODYNAMICS

- This law states that, 'it is impossible to convert heat into equal amount of work without compensation.'

Entropy (S)

- Entropy is defined as a measure of randomness or disorder of the system. It is denoted by S . The order of randomness or entropy of solid, liquid and gas is, Gas > Liquid > Solid

$$\Delta S = \frac{q_{rev}}{T}$$

- Entropy change of an ideal gas is given by

$$\Delta S = nC_v \ln \left(\frac{T_2}{T_1} \right) + nR \ln \left(\frac{V_2}{V_1} \right)$$

- Entropy change for n moles of an ideal gas is given

$$\text{by } \Delta S = nC_p \ln \left(\frac{T_2}{T_1} \right) - nR \ln \left(\frac{P_2}{P_1} \right)$$

Gibbs Free Energy (G)

- It is the net energy available to do useful work.
 $G = H - TS$
- **Standard free energy of a reaction :**
 $\Delta_r G^\circ = \sum \Delta_f G^\circ_{\text{products}} - \sum \Delta_f G^\circ_{\text{reactants}}$
- **Gibbs-Helmholtz equation :** $\Delta G = \Delta H - T\Delta S$
 $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$
- $\Delta G^\circ = -nFE^\circ$; where, E° is standard emf of cell.
- **Gibbs energy and spontaneity :** ΔG gives a criteria for spontaneity at constant pressure and temperature.
 - If $\Delta G < 0$, process is spontaneous.
 - If $\Delta G > 0$, process is non-spontaneous.
 - If $\Delta G = 0$, process is in equilibrium.

- **Effect of temperature on spontaneity of reactions:**

$\Delta_r H^\circ$	$\Delta_r S^\circ$	$\Delta_r G^\circ$	Description
-	+	-	Reaction spontaneous at all temperatures
-	-	- (at low T)	Reaction spontaneous at low temperature
-	-	+ (at high T)	Reaction non-spontaneous at high temperature
+	+	+ (at low T)	Reaction non-spontaneous at low temperature
+	+	- (at high T)	Reaction spontaneous at high temperature
+	-	+	Reaction non-spontaneous at all temperatures

- **Gibbs energy change and equilibrium :** Gibbs energy change, $\Delta_r G^\circ$ is related to the equilibrium constant of the reaction as

$$\Delta_r G^\circ = -2.303 RT \log K$$

Gibbs energy change and equilibrium

ΔG°	$\log K$	K	Comment
$\Delta G^\circ = 0$	$\log K = 0$	1	The equilibrium mixture contains comparable amounts of reactants and products ($K = 1$ for 1 M concentrations and 1 atm partial pressures)
$\Delta G^\circ < 0$	$\log K > 0$	$K > 1$	The equilibrium mixture is mainly products, exothermic reactions.
$\Delta G^\circ > 0$	$\log K < 0$	$K < 1$	The equilibrium mixture is mainly reactants, endothermic reactions.

THIRD LAW OF THERMODYNAMICS

- The entropy of any pure crystalline substance approaches zero as the temperature approaches absolute zero.

COMIC CAPSULE

What is Iron Man's favourite amusement park ride? The ferrous wheel.

- In case of solids,

$$\Delta S = \int_0^T \frac{C_p dT}{T} = C_p \ln T = 2.303 C_p \log T$$

where C_p is the heat capacity of the substance at constant pressure and is supposed to remain constant in the range 0 to T K.

PEEP INTO PREVIOUS YEARS

10. In which case change in entropy is negative?
 (a) $2H_{(g)} \rightarrow H_{2(g)}$
 (b) Evaporation of water
 (c) Expansion of a gas at constant temperature
 (d) Sublimation of solid to gas (NEET 2019)
11. For a reaction taking place in a container in equilibrium with its surroundings, the effect of temperature on its equilibrium constant K in terms of change in entropy is described by
 (a) with increase in temperature, the value of K for endothermic reaction increases because unfavourable change in entropy of the surroundings decreases
 (b) with increase in temperature, the value of K for exothermic reaction decreases because favourable change in entropy of the surroundings decreases
 (c) with increase in temperature, the value of K for exothermic reaction decreases because the entropy change of the system is positive
 (d) with increase in temperature, the value of K for endothermic reaction increases because the entropy change of the system is negative. (JEE Advanced 2017)
12. For a sample of perfect gas when its pressure is changed isothermally from p_i to p_f , the entropy change is given by
 (a) $\Delta S = nR \ln \left(\frac{p_f}{p_i} \right)$ (b) $\Delta S = nR \ln \left(\frac{p_i}{p_f} \right)$
 (c) $\Delta S = nRT \ln \left(\frac{p_f}{p_i} \right)$ (d) $\Delta S = RT \ln \left(\frac{p_i}{p_f} \right)$ (NEET-II 2016)

POINTS FOR EXTRA SCORING

- Work done when one calorie of heat is produced = 4.18 J.
- 1 Joule = 0.2390 cal, 1 calorie = 4.184 J, 1 K cal = 4.184 kJ, 1 L-atm = 101.3 J = 1.013×10^9 erg = 24.206 cal
- Joule-Thomson Effect** : Change of temperature produced when a gas is made to expand adiabatically from a region of high pressure to a region of extremely low pressure through a small jet.

$$\mu_{JT} = \left(\frac{\partial T}{\partial P} \right)_H = \frac{1}{C_p} \left[\frac{2a}{RT} - b \right];$$
 where, μ_{JT} is Joule-Thomson coefficient.
- Joule-Thomson effect is zero for an ideal gas i.e., when an ideal gas expands in vacuum, there is neither absorption nor evolution of heat i.e., $q = 0$.
- When an ideal gas undergoes expansion under adiabatic conditions in vacuum no change takes place in its internal energy i.e., $\left(\frac{\partial E}{\partial V} \right)_T = 0$
- Gibbs Helmholtz equations**

$$\Delta G = \Delta H + T \left[\frac{d(\Delta G)}{dT} \right]_P \text{ or } \frac{\Delta G - \Delta H}{T} = \left[\frac{d(\Delta G)}{dT} \right]_P$$

$$\text{or } -\Delta S = \left[\frac{d(\Delta G)}{dT} \right]_P \text{ or } -\Delta S = \left[\frac{d(-nFE_{\text{cell}})}{dT} \right]_P$$
 Thus, $\Delta S = nF \left[\frac{dE_{\text{cell}}}{dT} \right]_P$
- For molecules having nearly same molecular mass and nearly same heat capacity, a more symmetrical molecule has lower entropy than less symmetrical.
- During stretching of a rubber band, entropy decreases due to uncoiling of macromolecules to arrange in more ordered manner and during boiling of egg, entropy increases due to denaturation of proteins from helical form into random coiled structure.

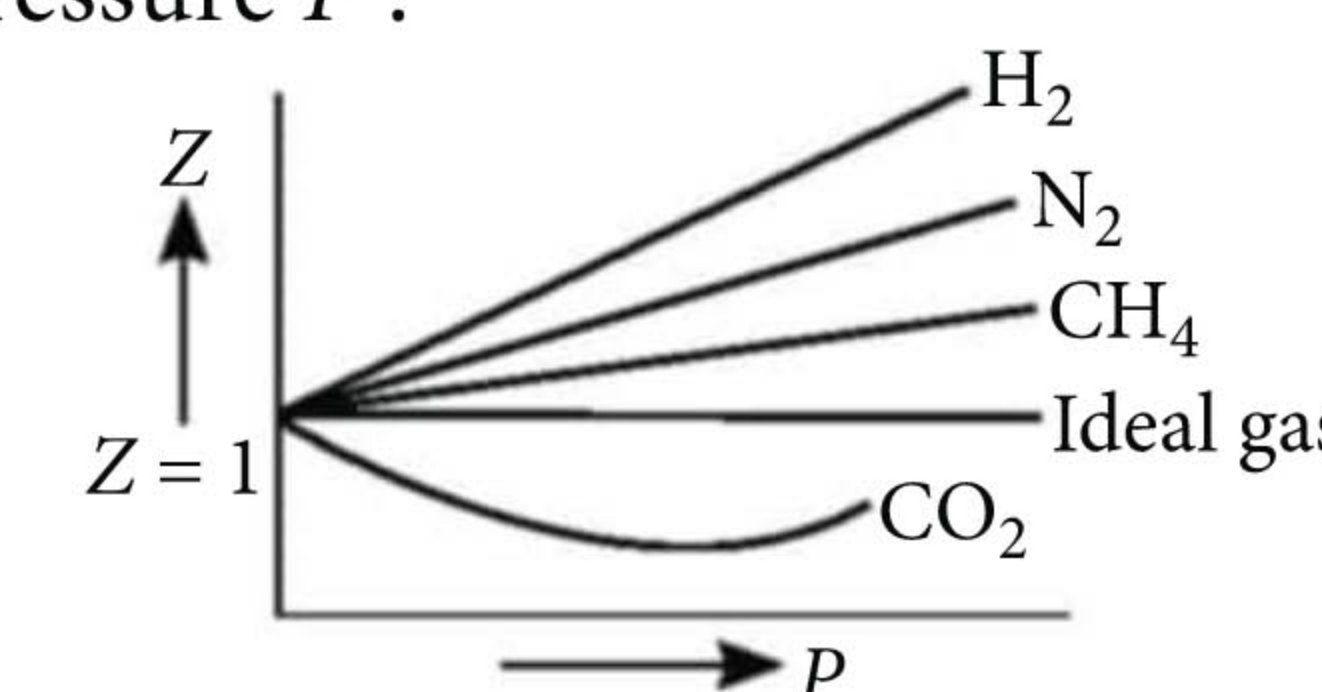
Answer Key For Peep Into Previous Years

- | | | | | | |
|--------|--------|--------|---------|------------|---------|
| 1. (d) | 2. (b) | 3. (c) | 4. (d) | 5. (a,c,d) | 6. (d) |
| 7. (b) | 8. (b) | 9. (b) | 10. (a) | 11. (a,b) | 12. (b) |



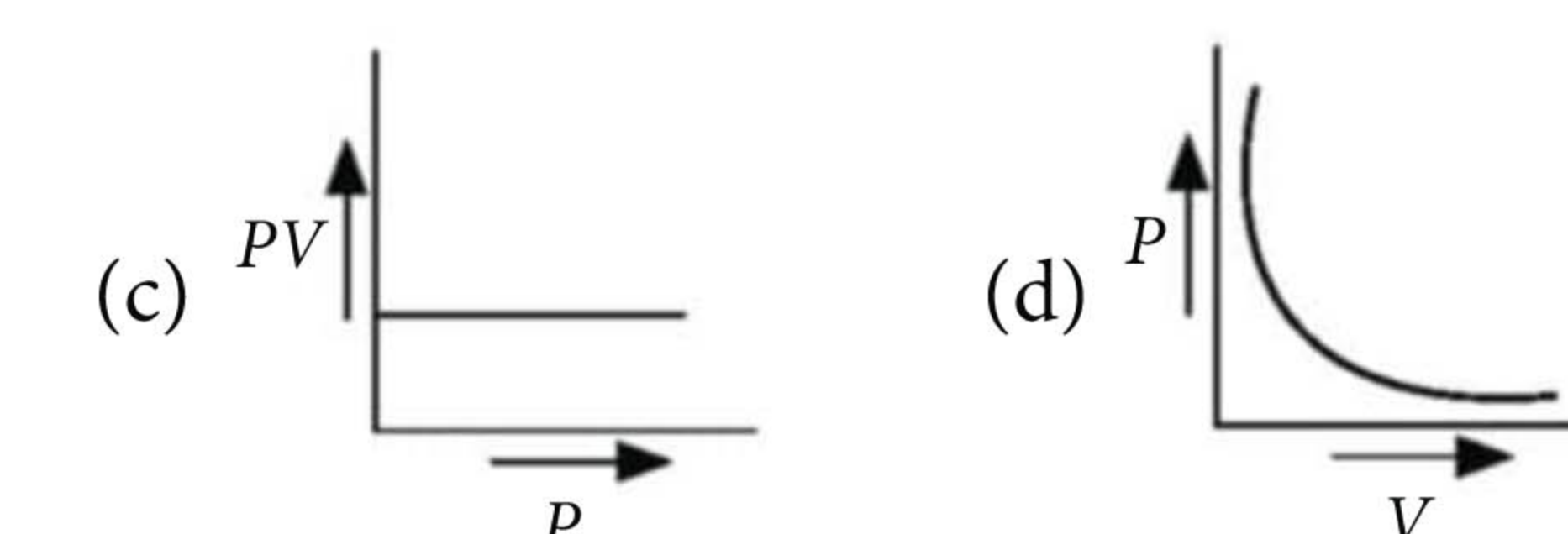
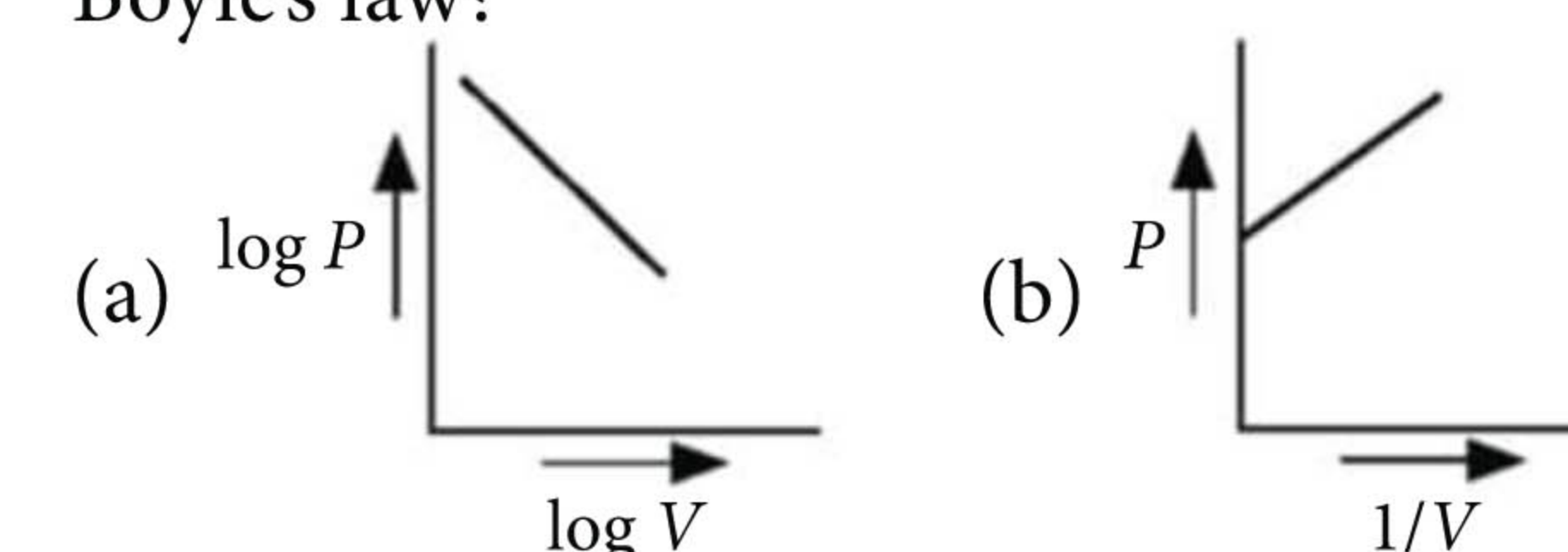
WRAP it UP

1. Consider the graph between compressibility factor Z and pressure P :



The correct increasing order of ease of liquefaction of the gases shown in the above graph is

- (a) $H_2 < N_2 < CH_4 < CO_2$
 (b) $CO_2 < CH_4 < N_2 < H_2$
 (c) $H_2 < CH_4 < N_2 < CO_2$
 (d) $CH_4 < H_2 < N_2 < CO_2$
2. Consider the following changes:
- 1 kg water (liquid at 25°C) $\xrightarrow{\Delta H_1}$ 1 kg water (liquid at 100°C) $\xrightarrow{\Delta H_2}$ 1 kg water (steam at 100°C)
- (Given : Specific heat of water = 1 cal/g °C
 Latent heat of vaporisation of water = 10 kcal/mol)
 ΔH_1 is
 (a) 75 kcal (b) 550 kcal (c) 750 kcal (d) 55 kcal
3. The pressure of 1 g of an ideal gas A at 27°C is 2 bar. When 2 g of another ideal gas B is added to the same flask at the same temperature, the pressure becomes 3 bar. The relationship between their molar masses is
 (a) $M_A = \frac{1}{4} M_B$ (b) $M_A = M_B$
 (c) $M_A = \frac{1}{2} M_B$ (d) $M_A = 4M_B$
4. Standard entropy of X_2 , Y_2 and XY_3 are 60, 40 and 50 J K⁻¹ mol⁻¹ respectively. For the reaction,
 $\frac{1}{2} X_2 + \frac{3}{2} Y_2 \rightarrow XY_3$, $\Delta H = -30$ kJ, to be at equilibrium, the temperature will be
 (a) 1250 K (b) 500 K (c) 750 K (d) 1000 K
5. Which of the following plots does not represent Boyle's law?



6. A process is non-spontaneous at every temperature if
 (i) $\Delta H > 0, \Delta S = 0$ (ii) $\Delta H < 0, \Delta S > 0$
 (iii) $\Delta H > 0, \Delta S < 0$ (iv) $\Delta H = 0, \Delta S < 0$
 (a) (i), (ii), (iii) (b) (ii), (iii), (iv)
 (c) (i), (ii), (iii), (iv) (d) (i), (iii), (iv)
7. What would be the number of moles of H_2 in 0.224 L of $H_{2(g)}$ at STP (273 K, 1 atm)? Assume the gas to behave ideally.
 (a) 0.001 (b) 0.1 (c) 1.0 (d) 0.01
8. The standard enthalpies of formation of $CO_{2(g)}$, $H_2O_{(l)}$, and glucose_(s) at 25°C are -400 kJ mol⁻¹, -300 kJ mol⁻¹ and -1300 kJ mol⁻¹ respectively. The standard enthalpy of combustion per gram of glucose at 25°C is
 (a) +16.11 kJ (b) -16.11 kJ
 (c) +2900 kJ (d) -2900 kJ
9. A neon (Ne)-dioxygen (O_2) mixture contains 160 g neon and 96 g dioxygen. If the pressure of the mixture of gases in the container is 30 bar, the partial pressure of neon and dioxygen in the mixture is
 (a) 21.9 bar, 8.1 bar (b) 17.3 bar, 12.7 bar
 (c) 15.7 bar, 14.3 bar (d) 18.9 bar, 11.1 bar.
10. For the process,
 $H_2O_{(l)} (1 \text{ bar}, 373 \text{ K}) \rightarrow H_2O_{(g)} (1 \text{ bar}, 373 \text{ K})$
 the correct set of thermodynamic parameters is
 (a) $\Delta G = -ve, \Delta S = +ve$ (b) $\Delta G = +ve, \Delta S = 0$
 (c) $\Delta G = 0, \Delta S = +ve$ (d) $\Delta G = 0, \Delta S = -ve$
11. Which of the following statements is not correct?
 (a) Viscosity of ethanol is lesser than that of glycol.
 (b) Viscosity of a liquid decreases with increase in temperature.
 (c) The variation of viscosity is given by $\eta = Ae^{(-E/RT)}$.
 (d) Capillary action is due to surface tension of a liquid.
12. One gram atom of graphite and one gram atom of diamond were separately burnt to carbon dioxide.

The amount of heat liberated were 393.5 kJ and 395.4 kJ respectively. It follows that

- graphite has greater affinity for oxygen
- diamond has greater affinity for oxygen
- graphite is stable than diamond
- diamond is stable than graphite.

13. If the average velocity of N_2 molecules is 0.3 m s^{-1} at 27°C , then the velocity of 0.6 m s^{-1} will take place at

- 273 K
- 927 K
- 1000 K
- 1200 K

14. Two moles of an ideal monoatomic gas expands isothermally against a constant external pressure of 2 atm from an initial volume of 22.4 L to a state where its final pressure becomes equal to external pressure. If the initial temperature of gas is 273°C , then the entropy change of the system in the above process is

- $R \ln 6$
- $R \ln 4$
- $R \ln 8$
- zero.

15. If Pd vs. P (where, P denotes pressure in atm and d denotes density in g/L) is plotted for He gas (assume ideal) at a particular temperature. If

$$\left[\frac{d}{dP} (Pd) \right]_{P=8.21 \text{ atm}} = 5, \text{ then the temperature will be}$$

- 160 K
- 320 K
- 80 K
- none of these.

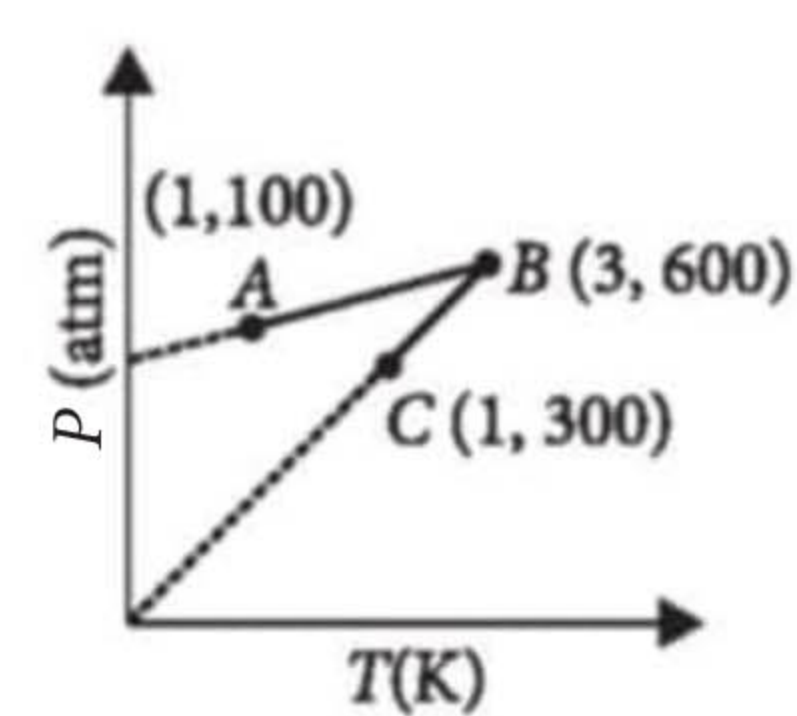
16. Which of the following is not a path function?

- q
 - w
 - q_v
 - $q + w$
- (i), (ii), (iii) and (iv)
 - Only (iii) and (iv)
 - Only (i) and (ii)
 - Only (i), (ii) and (iii)

17. At 400 K, the root mean square (u_{rms}) speed of a gas X (molecular weight = 40) is equal to the most probable speed (u_{mp}) of gas Y at 60 K. The molecular weight (g mol^{-1}) of the gas Y is

- 8
- 12
- 16
- 4

18. One mole of an ideal gas is subjected to a two step reversible process (A-B and B-C). The pressure at A and C is same. Mark the correct statement(s).



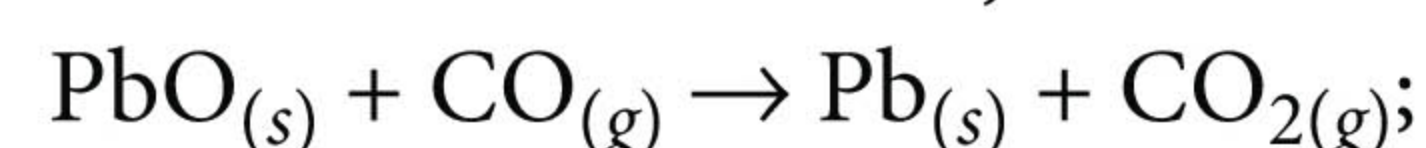
- Work involved in the path AB is zero.
- Volume of gas at A = volume of gas at B.
- Volume of gas at C = $3 \times$ volume of gas at A.
- Volume of gas at B is 25 litres.

19. The compression factor (compressibility factor) for 1 mole of a van der Waals' gas at 0°C and 100 atm pressure is found to be 0.5. Assuming that

the volume of a gas molecule is negligible, calculate the van der Waals' constant ' a '.

- $0.253 \text{ L}^2 \text{mol}^{-2} \text{ atm}$
- $0.53 \text{ L}^2 \text{mol}^{-2} \text{ atm}$
- $1.83 \text{ L}^2 \text{mol}^{-2} \text{ atm}$
- $1.253 \text{ L}^2 \text{mol}^{-2} \text{ atm}$

20. Consider the reaction,



$\Delta_f H^\circ = -65.69 \text{ kJ mol}^{-1}$. If $\Delta_f H^\circ$ for CO_2

and $\text{CO}_{(g)}$ are $-393.5 \text{ kJ mol}^{-1}$ and $-110.5 \text{ kJ mol}^{-1}$, respectively, calculate $\Delta_f H^\circ$ for $\text{PbO}_{(s)}$.

- $+217.3 \text{ kJ mol}^{-1}$
- $-317.2 \text{ kJ mol}^{-1}$
- $+317.2 \text{ kJ mol}^{-1}$
- $-217.3 \text{ kJ mol}^{-1}$

SOLUTIONS

1. (a): When $Z < 1$ the gas is said to show $-ve$ deviation. This implies that gas is more compressible and attractive forces predominate. Due to which liquefaction of the gas become easy. When $Z > 1$ the gas is said to show $+ve$ deviation. This means gas is less compressible. As the value of Z increases in graph, ease of liquefaction decreases.

2. (a): $\Delta H_1 = mC\Delta t = 1000 \times 1 \times 75 = 75000 \text{ cal} = 75 \text{ kcal}$

3. (a): According to data,

$$P_A = 2 \text{ bar} \quad P_B = 1 \text{ bar}$$

$$m_A = 1 \text{ g} \quad m_B = 2 \text{ g}$$

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According to the ideal gas equation, $PV = nRT$, we have

$$P_A V = n_A RT \quad \dots(i)$$

$$P_B V = n_B RT \quad \dots(ii)$$

On dividing the equations (i) and (ii), we get

$$\frac{P_A}{P_B} = \frac{n_A}{n_B} = \frac{m_A}{M_A} \times \frac{M_B}{m_B} = \frac{m_A}{m_B} \times \frac{M_B}{M_A}; \quad \frac{2 \text{ bar}}{1 \text{ bar}} = \frac{1 \text{ g}}{2 \text{ g}} \times \frac{M_B}{M_A}$$

$$\text{Thus, } M_A = \frac{1}{4} M_B$$

4. (c): $\Delta S = S_{\text{Product}} - S_{\text{Reactant}}$

$$\Delta S = S_{(XY_3)} - \left(\frac{1}{2} S_{(X_2)} + \frac{3}{2} S_{(Y_2)} \right)$$

$$= 50 - (30 + 60) = -40 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\Delta H = -30 \text{ kJ} = -30000 \text{ J}$$

$$\Delta G = \Delta H - T\Delta S$$

At equilibrium, $\Delta G = 0$

$$T = \frac{\Delta H}{\Delta S} = \frac{-30000}{-40} = 750 \text{ K}$$

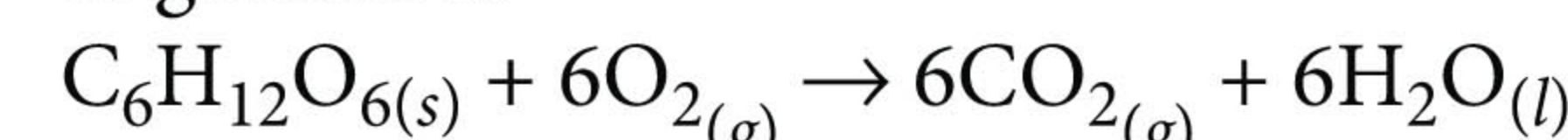
5. (b)

6. (d)

7. (d): n_{H_2} = Volume of $H_{2(g)}$ of STP/22.4 L mol^{-1}

$$= 0.224 \text{ L}/22.4 \text{ L mol}^{-1} = 0.01 \text{ mol}$$

8. (b): Thermochemical equation for the combustion of glucose is



According to thermodynamics,

$$\Delta_r H^\circ = \sum a_i \Delta_f H^\circ_{(\text{Products})} - \sum b_i \Delta_f H^\circ_{(\text{Reactants})}$$

$$\Delta_c H^\circ = [(6 \text{ mol}) \Delta_f H^\circ_{\text{CO}_{2(g)}} + (6 \text{ mol}) \Delta_f H^\circ_{\text{H}_2\text{O}_{(l)}}]$$

$$- [(1 \text{ mol}) \Delta_f H^\circ_{\text{C}_6\text{H}_{12}\text{O}_{6(s)}} + (6 \text{ mol}) \Delta_f H^\circ_{\text{O}_{2(g)}}]$$

$$= [6(-400) + 6(-300)] - (-1300) = -2900 \text{ kJ mol}^{-1}$$

\therefore Enthalpy of combustion per gram of glucose

$$= \frac{-2900 \text{ kJ mol}^{-1}}{180 \text{ g mol}^{-1}} = -16.11 \text{ kJ}$$

(molar mass of glucose = 180 g mol^{-1})

9. (a): $n_{\text{Ne}} = \frac{\text{Mass}_{\text{Ne}}}{\text{Molar mass}_{\text{Ne}}} = \frac{160 \text{ g}}{20 \text{ g mol}^{-1}} = 8 \text{ mol}$

$$n_{\text{O}_2} = \frac{\text{Mass}_{\text{O}_2}}{\text{Molar mass}_{\text{O}_2}} = \frac{96 \text{ g}}{32 \text{ g mol}^{-1}} = 3 \text{ mol}$$

$$x_{\text{Ne}} = \frac{n_{\text{Ne}}}{n_{\text{Ne}} + n_{\text{O}_2}} = \frac{8}{8+3} = \frac{8}{11} = 0.73$$

As $p_i = x_i P_{\text{total}}$

$$\therefore p_{\text{Ne}} = P_{\text{total}} \cdot x_{\text{Ne}} = (0.73) (30 \text{ bar}) = 21.9 \text{ bar}$$

$$p_{\text{O}_2} = P_{\text{total}} - p_{\text{Ne}} = 30 \text{ bar} - 21.9 \text{ bar} = 8.1 \text{ bar}$$

10. (c): At the transition temperature (that is, at the boiling point), the system is at equilibrium. Therefore,

$\Delta G = 0$. Due to the conversion of liquid into vapour, the randomness of the system increases. Thus, ΔS is positive (> 0).

11. (c)

12. (c): Since graphite on combustion gives less heat, it means graphite has less heat content and is more stable.

13. (d): According to the kinetic molecular theory of

$$\text{gases, } u_{av} = \sqrt{\frac{8RT}{\pi M}} \text{ i.e., } u_{av} \propto \sqrt{T} \quad \therefore \frac{(u_{av})_1}{(u_{av})_2} = \sqrt{\frac{T_1}{T_2}}$$

$$\frac{0.3 \text{ m s}^{-1}}{0.6 \text{ m s}^{-1}} = \sqrt{\frac{(27+273)}{T_2}} \Rightarrow \frac{1}{2} = \sqrt{\frac{300}{T_2}} \text{ or } \frac{1}{4} = \frac{300}{T_2}$$

or $T_2 = 1200 \text{ K}$

14. (b): For initial state, $P_i \times 22.4 = 2 \times R \times 546$

$$\therefore P_i = 4 \text{ atm}$$

Now, $P_i V_i = P_f V_f$ (\because process is isothermal)

$$4 \times 22.4 = 2 \times V_f \quad \therefore V_f = 44.8 \text{ L}$$

$$\therefore \Delta S_{\text{sys}} = nR \ln \left(\frac{V_f}{V_i} \right) = 2R \ln \left(\frac{44.8}{22.4} \right) = 2R \ln 2 = R \ln 4$$

$$15. (a): PM = dRT; Pd = P^2 \left(\frac{M}{RT} \right); \frac{d(Pd)}{dP} = \frac{2PM}{RT}$$

$$5 = \frac{2 \times 8.21 \times 4}{0.0821 \times T}; T = 160 \text{ K}$$

16. (b): Although neither heat nor work is a state function but their sum ($q + w$) is equal to ΔU and U is a state function. Similarly, q_v (molar heat capacity at constant volume) is a state function as it is equal to ΔU .

17. (d): $u_{rms} = u_{mp}$

$$\sqrt{\frac{3RT}{M_{(X)}}} = \sqrt{\frac{2RT'}{M_{(Y)}}} \Rightarrow \sqrt{\frac{3R \times 400}{40}} = \sqrt{\frac{2R \times 60}{M_{(Y)}}}$$

$$\Rightarrow M_{(Y)} = 4$$

18. (c): $V_A = \frac{1 \times R \times 100}{1} = 100 \text{ R}$

$$V_B = \frac{1 \times R \times 600}{3} = 200 \text{ R}; V_C = \frac{1 \times R \times 300}{1} = 300 \text{ R}$$

$\therefore V_B > V_A$, so expansion of gas takes place.

$$V_B = 200 \times 0.0821 = 16.42 \text{ L}$$

Monthly Test Drive CLASS XII ANSWER KEY

- | | | | | |
|-------------|-------------|---------------|---------|-------------|
| 1. (b) | 2. (a) | 3. (a) | 4. (d) | 5. (b) |
| 6. (c) | 7. (d) | 8. (d) | 9. (c) | 10. (b) |
| 11. (d) | 12. (b) | 13. (c) | 14. (c) | 15. (d) |
| 16. (b) | 17. (b) | 18. (a) | 19. (a) | 20. (a,b,c) |
| 21. (a,b,c) | 22. (a,b,c) | 23. (a,b,c,d) | | |
| 24. (5) | 25. (1) | 26. (4) | 27. (a) | 28. (c) |
| 29. (a) | 30. (c) | | | |

19. (d): We know that

$$Z = \frac{PV}{RT} \Rightarrow 0.5 = \frac{100 \times V}{0.0821 \times 273} \Rightarrow V = 0.112 \text{ litre}$$

According to van der Waals' equation,

$$\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = RT$$

$$\left(100 + \frac{a}{(0.112)^2}\right)(0.112 - 0) = 0.0821 \times 273$$

$$a = 1.253 \text{ L}^2 \text{mol}^{-2} \text{ atm}$$

20. (d): According to the mathematical form of Hess's law, we have

$$\Delta_r H^\circ = \sum_i a_i \Delta_f H^\circ(\text{products}) - \sum_i b_i \Delta_f H^\circ(\text{reactants})$$

$$\Delta_f H^\circ = [\Delta_f H^\circ_{\text{Pb(s)}} + \Delta_f H^\circ_{\text{CO}_2(\text{g})}] - [\Delta_f H^\circ_{\text{PbO(s)}} + \Delta_f H^\circ_{\text{CO(g)}}]$$

$$-65.69 \text{ kJ mol}^{-1} = [0 + (-393.5 \text{ kJ mol}^{-1})] - [\Delta_f H^\circ_{\text{PbO(s)}} + (-110.5 \text{ kJ mol}^{-1})]$$

$$\Rightarrow \Delta_f H^\circ_{\text{PbO(s)}} = (65.69 - 393.5 + 110.5) \text{ kJ mol}^{-1}$$

$$= -217.3 \text{ kJ mol}^{-1}$$



Science Behind Indian Customs

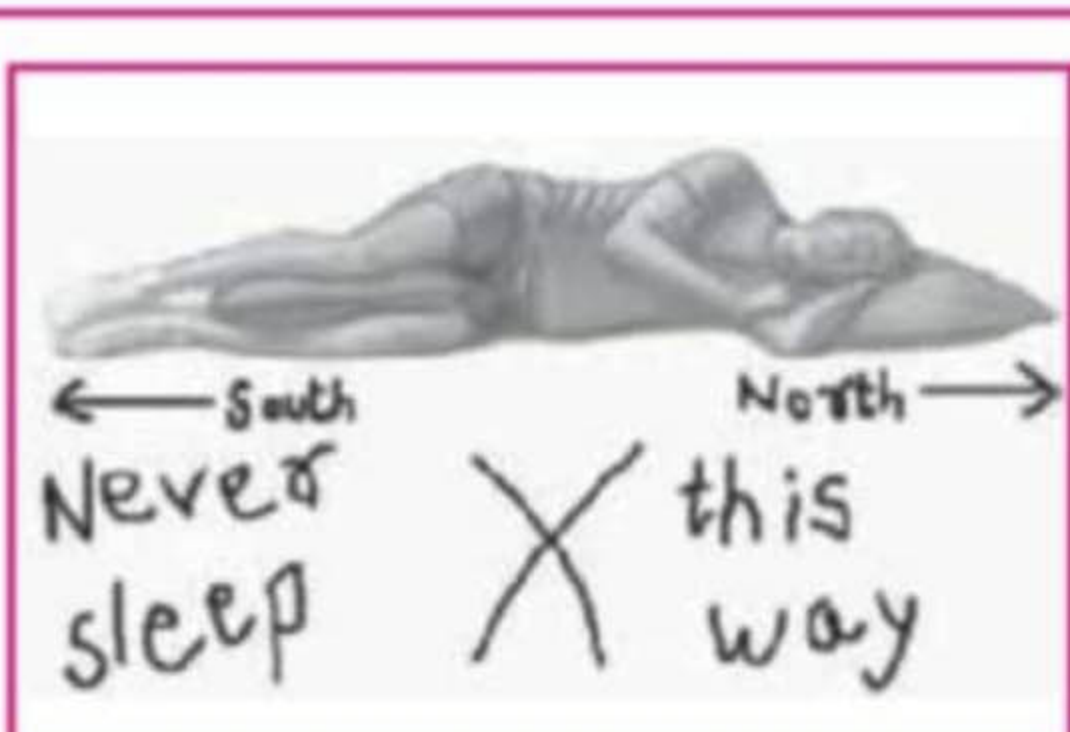


Sitting on a floor and eating

This tradition is not just about sitting on floor and eating, it is regarding sitting in the "Sukhasan" position and then eating. Sukhasan is the position we normally use for Yoga asanas. Sitting in this position while eating helps in improving digestion as the circulatory system can focus solely upon digestion and not on our legs dangling from a chair or supporting us while we are standing.

Why not to sleep with your head towards North?

Myth is that it invites ghost or death but since says that it is because human body has its own magnetic field (Also known as hearts magnetic field, because the flow of blood) and Earth is a giant magnet. When we sleep with head towards north, our body's magnetic field become completely asymmetrical to the Earth's Magnetic field. That cause problems related to blood pressure and our heart needs to work harder in order to overcome this asymmetry of Magnetic fields.

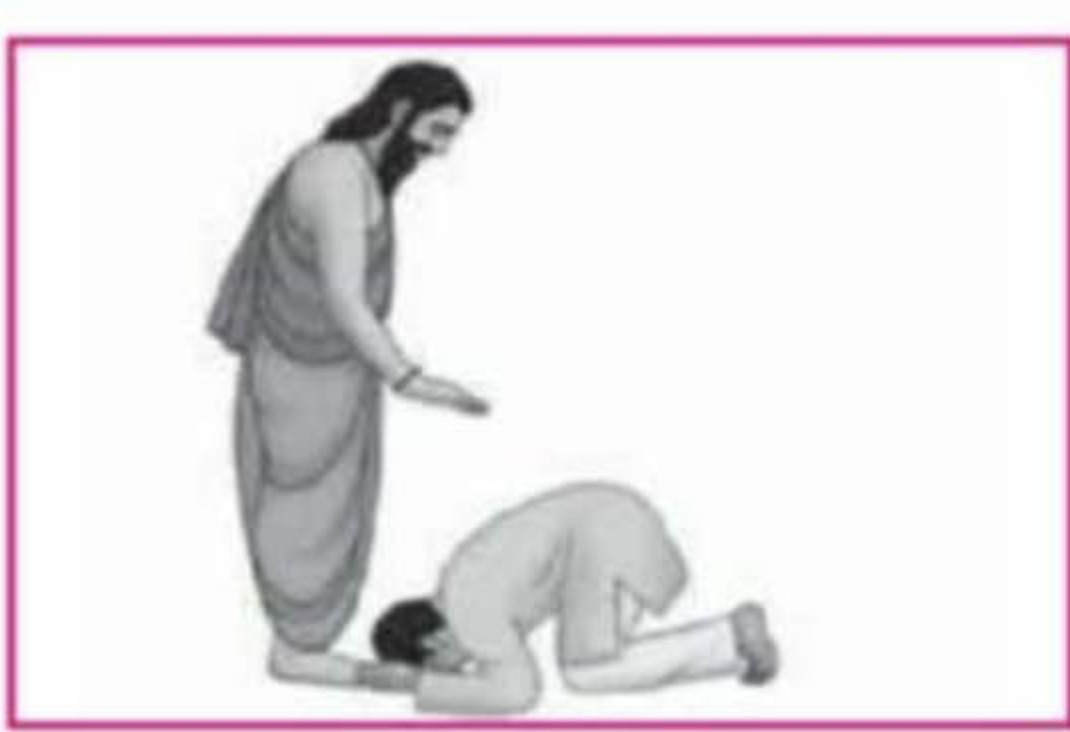


Surya Namaskar

Hindus have a tradition of paying regards to Sun God early in the morning by their water offering ritual. It was mainly because looking at Sun rays through water or directly at that time of the day is good for eyes and also by waking up to follow this routine, we become prone to a morning lifestyle and mornings are proven to be the most effective part of the day.

Touching feet (charan-sparsh)

Usually, the person of whose feet you are touching is either old or pious. When they accept your respect which came from your reduced ego (and is called your shraddha) their hearts emit positive thoughts and energy (which is called their karuna) which reaches you through their hands and toes. In essence, the completed circuit enables flow of energy and increases cosmic energy, switching on a quick connect between two minds and hearts. To an extent, the same is achieved through handshakes and hugs.



Why do we fast?

The underlying principle behind fasting is to be found in Ayurveda. This ancient Indian medical system sees the basic cause of many diseases as the accumulation of toxic materials in the digestive system. Regular cleansing of toxic materials keeps one healthy. By fasting, the digestive organs get rest and all body mechanisms are cleansed and corrected. A complete fast is good for health, and the occasional intake of warm lemon juice during the period of fasting prevents the flatulence.



CBSE warm-up!

CLASS-X

Chapterwise practice questions for CBSE Exams as per the latest pattern and marking scheme issued by CBSE for the academic session 2019-20.

Series 3

States of Matter (Gaseous and Liquids) | Thermodynamics

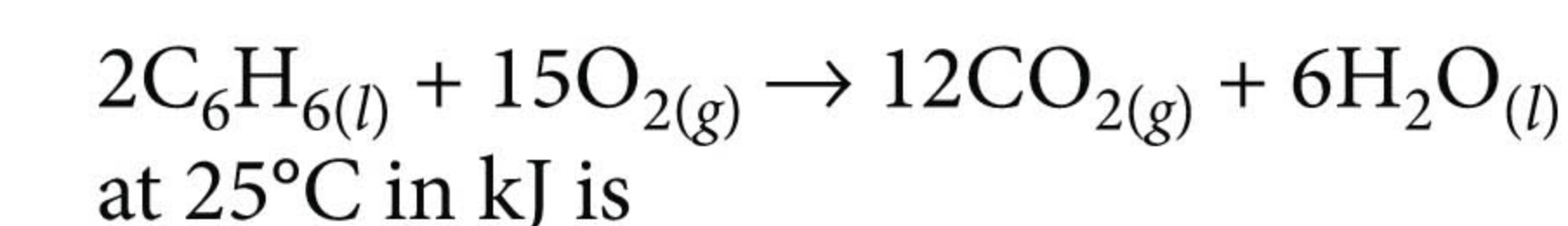
Time Allowed : 3 hours
Maximum Marks : 70

GENERAL INSTRUCTIONS

- All questions are compulsory.
- Section A : Q. no. 1 to 20 are very short answer-objective questions and carry 1 mark each.
- Section B : Q. no. 21 to 27 are short answer questions and carry 2 marks each.
- Section C : Q. no. 28 to 34 are long answer-I questions and carry 3 marks each.
- Section D : Q. no. 35 to 37 are long answer-II questions and carry 5 marks each.
- There is no overall choice in the question paper. However, internal choices are given in the sections.
- Use log tables if necessary, use of calculators is not allowed.

SECTION - A

- Molar heat capacity of water in equilibrium with ice at constant pressure is
(a) zero (b) infinity
(c) 40.45 kJ K⁻¹ mol⁻¹ (d) 75.48 kJ K⁻¹ mol⁻¹
- The enthalpy change for a reaction does not depend upon the
(a) physical states of reactants and products
(b) use of different reactants for the same product
(c) nature of intermediate reaction steps
(d) difference in initial or final temperatures of involved substances.
- At 27°C, 500 mL of helium diffuses in 30 minutes. What is the time (in hours) taken for 1000 mL of SO₂ to diffuse under the same experimental conditions?
(a) 10 (b) 3
(c) 2 (d) 4
- The difference between heats of reaction at constant pressure and constant volume for the reaction,

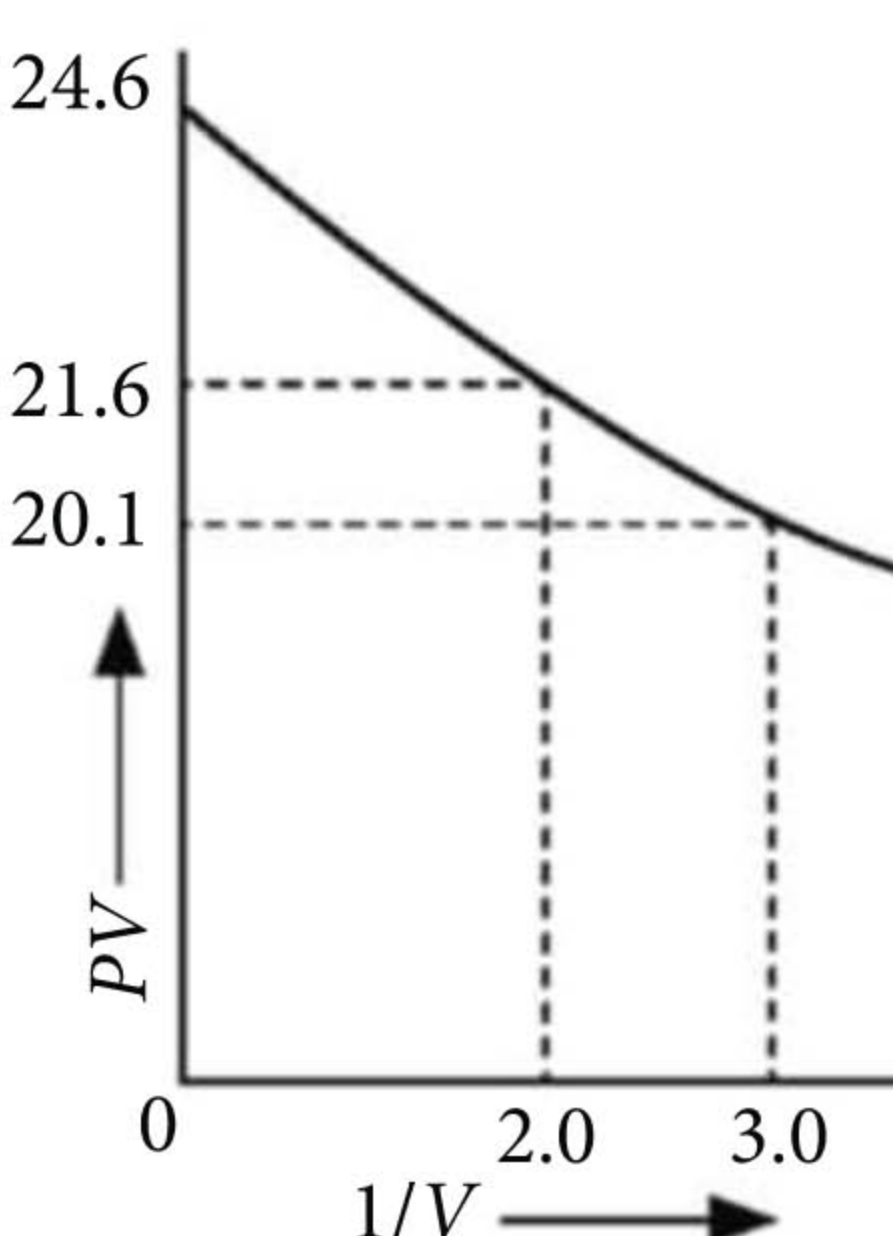


- (a) -7.43 (b) +3.72
(c) -3.72 (d) +7.43

- For a monoatomic gas, kinetic energy = E . The relation with rms velocity is
(a) $u = (2E/M)^{1/2}$ (b) $u = (3E/2M)^{1/2}$
(c) $u = (E/2M)^{1/2}$ (d) $u = (E/3M)^{1/2}$
- The compressibility of gas is less than unity at STP. Therefore,
(a) $V_m > 22.4$ litres (b) $V_m < 22.4$ litres
(c) $V_m = 22.4$ litres (d) $V_m = 44.8$ litres
- Which of the following reaction, defines $\Delta_f H^\circ$?
(a) $\text{C}_{(\text{diamond})} + \text{O}_{2(g)} \rightarrow \text{CO}_{2(g)}$
(b) $\frac{1}{2}\text{H}_{2(g)} + \frac{1}{2}\text{F}_{2(g)} \rightarrow \text{HF}_{(g)}$
(c) $\text{N}_{2(g)} + 3\text{H}_{2(g)} \rightarrow 2\text{NH}_{3(g)}$
(d) $\text{CO}_{(g)} + \frac{1}{2}\text{O}_{2(g)} \rightarrow \text{CO}_{2(g)}$

8. A heat engine absorbs heat Q_1 at temperature T_1 and heat Q_2 at temperature T_2 . Work done by the engine is $J(Q_1 + Q_2)$. This data
- violates 1st law of thermodynamics
 - violates 1st law of thermodynamics if Q_1 is -ve
 - violates 1st law of thermodynamics if Q_2 is -ve
 - does not violate 1st law of thermodynamics.

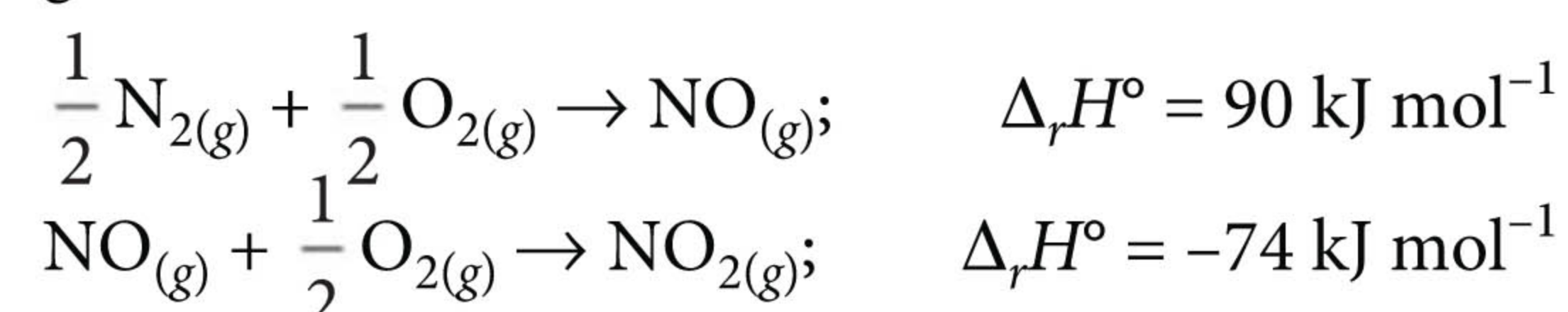
9. For one mole of a van der Waals' gas when $b = 0$ and $T = 300$ K, the PV vs $1/V$ plot is as shown in the diagram. The value of van der Waals' constant a ($\text{atm litre}^2 \text{ mol}^{-2}$) is



- 1.0
 - 4.5
 - 1.5
 - 3.0
10. An ideal gas is allowed to expand both reversibly and irreversibly in an isolated system. If T_i is the initial temperature and T_f is the final temperature, which of the following statements is correct?
- $(T_f)_{\text{rev}} = (T_f)_{\text{irrev}}$
 - $T_f = T_i$ for both reversible and irreversible processes
 - $(T_f)_{\text{irrev}} > (T_f)_{\text{rev}}$
 - $T_f > T_i$ for reversible process but $T_f = T_i$ for irreversible process
11. Calculate the root mean square velocity of ozone kept in a closed vessel at 20°C and 82 cm mercury pressure.
12. When an ideal gas expands into vacuum, there is neither absorption nor evolution of heat. Why?
13. Why do we see a white cloud like trail coming out of the high flying jet?
14. Predict the sign of ΔS° for the following reaction :
 $2\text{H}_2\text{S}_{(\text{g})} + 3\text{O}_{2(\text{g})} \rightarrow 2\text{H}_2\text{O}_{(\text{g})} + 2\text{SO}_{2(\text{g})}$
 (NCT 2011, 2017)
15. Which of the following are state functions?
- Height of a hill
 - Distance travelled in climbing the hill
 - Energy consumed in climbing the hill
16. The first law of thermodynamics is not adequate in predicting the direction of the process. Is it true or false?
17. 'Equal volumes of gases contain equal number of atoms', is true at what conditions?

18. Calculate Boyle's temperature for CO_2 gas. Given that $a = 3.59 \text{ L}^2 \text{ atm mol}^{-2}$ and $b = 0.0427 \text{ L mol}^{-1}$.

19. Comment on the thermodynamic stability of $\text{NO}_{(\text{g})}$, given

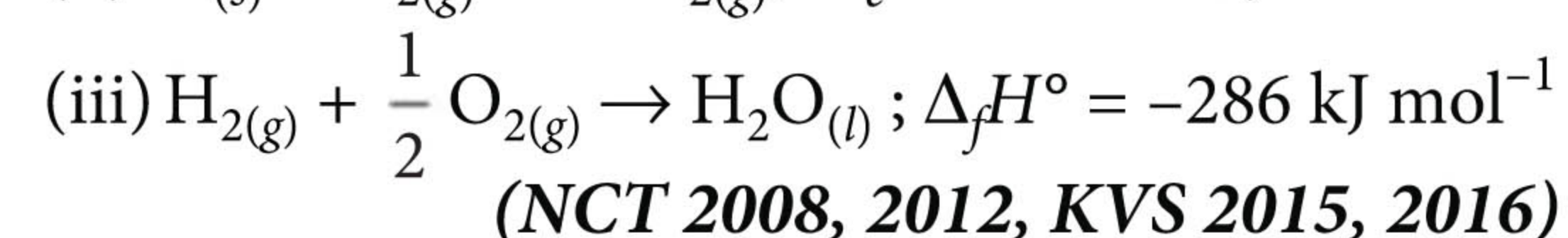
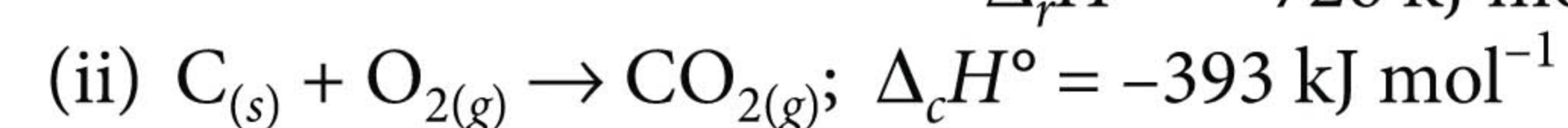
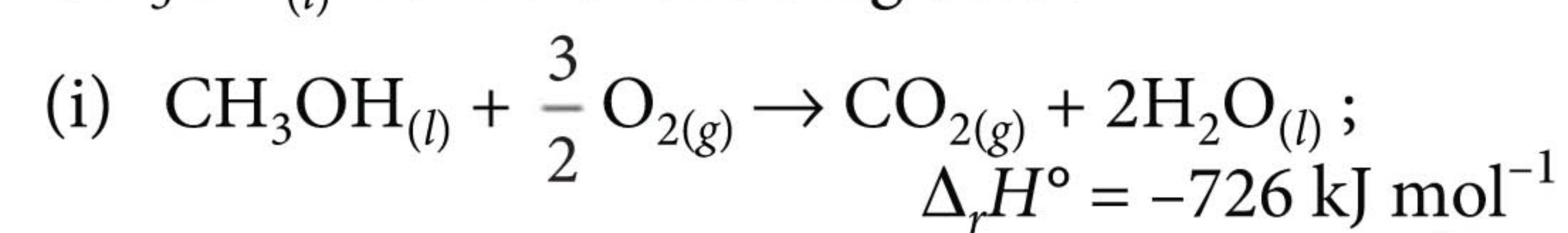


20. At 1 atm, will $\Delta_f H^\circ$ be zero for $\text{Cl}_{2(\text{g})}$ and $\text{Br}_{2(\text{g})}$? Explain.

SECTION - B

21. The drain cleaner, Drainex contains small bits of aluminium which reacts with caustic soda to produce hydrogen. What volume of hydrogen at 20°C and one bar will be released when 0.15 g of aluminium reacts? ($R = 0.083 \text{ L bar mol}^{-1} \text{ K}^{-1}$)

22. Calculate standard enthalpy of formation of $\text{CH}_3\text{OH}_{(\text{l})}$ from the following data :



23. The heat energy, q , absorbed by a gas is equal to ΔH is true at what condition(s)?

OR

Standard vaporization enthalpy of benzene at boiling point is 30.8 kJ mol^{-1} . For how long would 100 W electric heater have to operate in order to vaporize 100 g benzene at that temperature? (Power = Energy/Time and $1 \text{ W} = 1 \text{ J s}^{-1}$).

24. Calculate the density of NH_3 at 30°C and 5 atm pressure.

25. 20% N_2O_4 molecules are dissociated in a sample of a gas at 27°C and 760 torr. Calculate the density of equilibrium mixture.

26. The standard enthalpies of formation of O_3 , CaO , NH_3 and HI are $+142.2 \text{ kJ}$, -634.9 kJ , -46 kJ and $+25.95 \text{ kJ}$ respectively. Arrange them in order of their increasing stability with respect to decomposition into their elements.

OR

- (a) Calculate the energy needed to raise the temperature of 10.0 g of iron from 25°C to 500°C , if specific heat capacity of iron is $0.45 \text{ J}^\circ\text{C}^{-1} \text{ g}^{-1}$.

- (b) Write the conditions in terms of ΔH and ΔS when a reaction would be always spontaneous.

27. (i) Critical temperature for CO_2 and CH_4 are 31.1°C and -81.9°C respectively. Which of these has stronger intermolecular forces and why?

- (ii) Explain the significance of the van der Waals' parameters.

SECTION - C

28. One mole of a perfect gas undergoes the following processes:

- a reversible isobaric expansion from (1.0 atm, 20.0 L) to (1.0 atm, 40.0 L).
- a reversible isochoric change of state from (1.0 atm, 40.0 L) to (0.5 atm, 40.0 L).
- a reversible isothermal compression from (0.5 atm, 40.0 L) to (1.0 atm, 20.0 L).

Calculate the total work (w), total heat change (q) and ΔU involved in the above processes.

29. 4.215 g of a metallic carbonate was heated in a hard glass tube and the CO_2 evolved was found to measure 1336 mL at 27°C and 700 mm pressure. What is the equivalent weight of the metal?

OR

A straight glass tube has two inlets X and Y at the two ends. The length of the tube is 200 cm. HCl gas through inlet X and NH_3 gas through inlet Y are allowed to enter the tube at the same time. White fumes appear at a point P inside the tube. Find the distance of P from X.

30. 2.9 g of a gas at 95°C occupied the same volume as 0.184 g of dihydrogen at 17°C at the same pressure. What is the molar mass of the gas?

(NCERT, NCT 2010, KVS 2016)

31. Answer the following :

- What is compressibility factor Z?
- What is the value of Z for an ideal and non-ideal gas?
- For real gas what will be the effect on value of Z above Boyle's temperature?

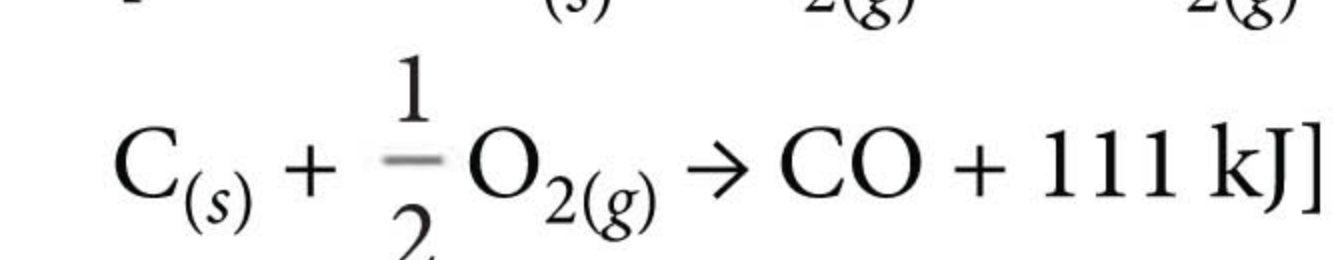
32. Given the following standard heats of reactions:

- heat of formation of water = -68.3 kcal ;
 - heat of combustion of acetylene = -310.6 kcal ;
 - heat of combustion of ethylene = -337.2 kcal ;
- Calculate the heat of reaction for the hydrogenation of acetylene at constant volume (25°C).

OR

In an oven using coal (assume the coal is 80% carbon in weight), insufficient oxygen is supplied such that 60% of carbon is converted to CO_2 and 40% carbon is converted to CO. Find out the heat generated when 10 kg of coal is burnt in this fashion.

[Given : $\text{C}_{(\text{s})} + \text{O}_{2(\text{g})} \rightarrow \text{CO}_{2(\text{g})} + 394 \text{ kJ}$



33. Answer the following :

- In terms of Charles' law explain why -273°C is the lowest possible temperature?
- A balloon filled with an ideal gas is taken from the surface of the sea deep to a depth of 100 m. What will be its volume in terms of its original volume?

34. Answer the following :

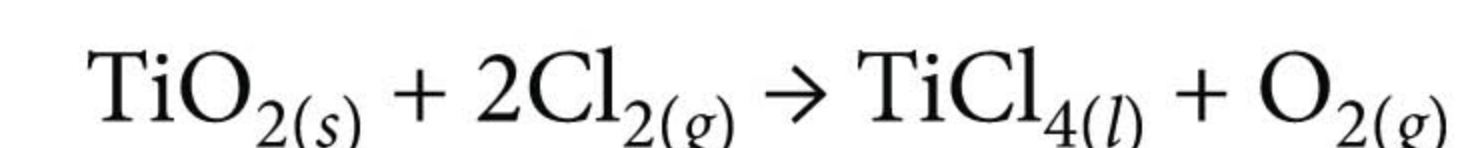
- When 60 g of iron was burnt to ferric oxide at constant pressure, energy equivalent to 43.9 kJ was evolved. Find the enthalpy of formation of ferric oxide. (Atomic mass of iron = 56.)
- The enthalpy change (ΔH) for the reaction, $\text{N}_{2(\text{g})} + 3\text{H}_{2(\text{g})} \rightarrow 2\text{NH}_{3(\text{g})}$ is $-92.38 \text{ kJ mol}^{-1}$ at 298 K. What is ΔU at 298 K?

SECTION - D

35. (a) Calculate the work done when 11.2 g of iron dissolves in hydrochloric acid in

- a closed vessel
- an open beaker at 25°C .
(Atomic mass of Fe = 56 u)

- (b) Titanium metal is extensively used in aerospace industry because the metal imparts strength to the structures but does not unduly add to their masses. The metal is produced by the reduction of $\text{TiCl}_{4(\text{l})}$ which, in turn, is produced from mineral rutile, $\text{TiCl}_{2(\text{s})}$. Can the following reduction for the production of $\text{TiCl}_{4(\text{l})}$ be carried out at 25°C ?



Given that H_f for $\text{TiO}_{2(\text{s})}$, $\text{TiCl}_{4(\text{l})}$, $\text{Cl}_{2(\text{g})}$ and $\text{O}_{2(\text{g})}$ are $-944.7 \text{ kJ mol}^{-1}$, $-804.2 \text{ kJ mol}^{-1}$, 0 kJ mol^{-1} and 0 kJ mol^{-1} . Also, S° for $\text{TiO}_{2(\text{s})}$, $\text{TiCl}_{4(\text{l})}$, $\text{Cl}_{2(\text{g})}$ and $\text{O}_{2(\text{g})}$ are 50.3 J mol^{-1} , 252.3 J mol^{-1} , 233.0 J mol^{-1} and 205.1 J mol^{-1} respectively.

OR

- (a) Fill up the blanks in the following table related to $\text{H}_2\text{O}_{(l)} \rightarrow \text{H}_2\text{O}_{(\text{steam})}$ at standard atmospheric pressure.

S. No.	$t^\circ\text{C}$	$T\text{K}$	ΔH (Enthalpy change) kJ mol^{-1}	ΔS (Entropy change) $\text{J mol}^{-1}\text{K}^{-1}$	$T\Delta S$ kJ	ΔG (Free energy) kJ
1.	90	363.0	41.1	—	—	+1.193
2.	110	373.3	40.7	109	—	—
3.	110	383.0	40.1	—	—	-0.979

- (b) Calculate $\Delta_f H^\circ$ for the process at 25°C of dissolving 1.00 mol of KCl in a large excess of water. Does this process represent an ionisation reaction? Explain.

$$\Delta_f H^\circ [\text{K}^+_{(\text{aq})}] = -251.2 \text{ kJ mol}^{-1}$$

$$\Delta_f H^\circ [\text{Cl}^-_{(\text{aq})}] = -167.08 \text{ kJ mol}^{-1}$$

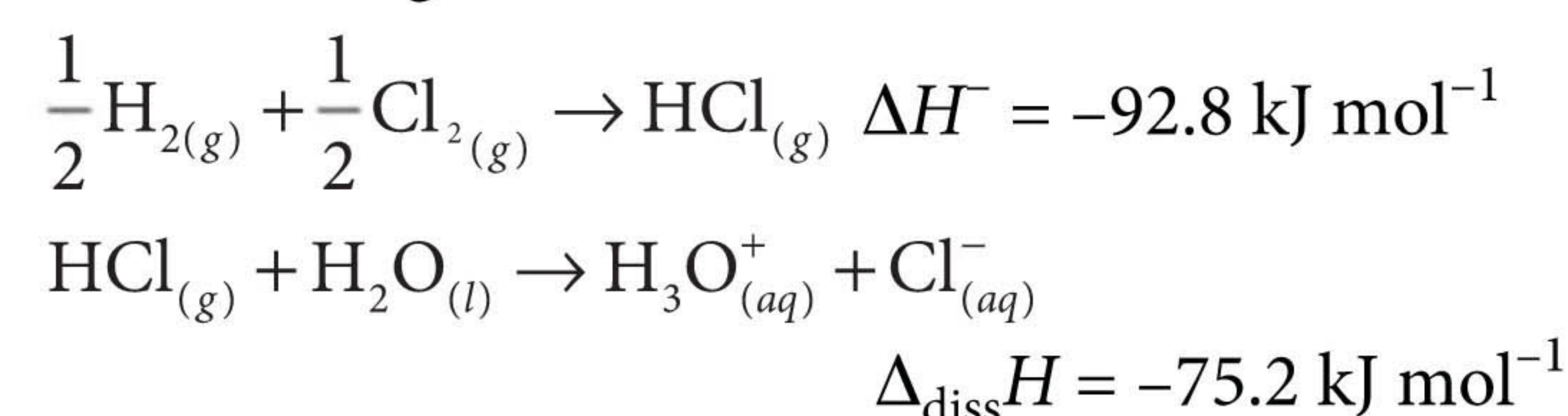
$$\Delta_f H^\circ [\text{KCl}] = -437.6 \text{ kJ mol}^{-1}$$

36. A 20.0 cm^3 mixture of CO , CH_4 and He gases is exploded by an electric discharge at room temperature with excess of oxygen. The volume contraction is found to be 13.0 cm^3 . A further contraction of 14.0 cm^3 occurs when the residual gas is treated with KOH solution. Find out the composition of the gaseous mixture in terms of volume percentage.

OR

- (a) Pressure of 1 g of an ideal gas at 27°C is found to be 2 bar. When 2 g of another ideal gas B is introduced in the same flask at the same temperature, the pressure becomes 3 bar. Find the relationship between their molecular masses.
- (b) An LPG cylinder weighs 14.8 kg when empty. When full, it weighs 29.0 kg and shows a pressure of 2.5 atm. In the course of use at 27°C , the mass of the full cylinder is reduced to 23.2 kg. Find out the volume of the gas in cubic metres used up under the normal usage conditions and the final pressure inside the cylinder. Assume LPG to be n -butane with normal boiling point of 0°C .
37. (a) Calculate the enthalpy change on freezing of 1.0 mol of water at 10.0°C to ice at -10.0°C .
 $\Delta_{\text{fus}} H = 6.03 \text{ kJ mol}^{-1}$ at 0°C .
 $C_p[\text{H}_2\text{O}_{(l)}] = 75.3 \text{ J mol}^{-1}\text{K}^{-1}$
 $C_p[\text{H}_2\text{O}_{(s)}] = 36.8 \text{ J mol}^{-1}\text{K}^{-1}$

- (b) Calculate $\Delta_f H^\circ$ for chloride ion from the following data:



OR

- (a) Define system and surroundings. What is an adiabatic process?
- (b) A chemist while studying the properties of gaseous $\text{C}_2\text{Cl}_2\text{F}_2$, a chlorofluorocarbon refrigerant, cooled a 1.25 g sample at constant atmospheric pressure of 1.0 atm from 320 K to 293 K. During cooling, the sample volume decreased from 274 to 248 mL. Calculate ΔH and ΔU of the chlorofluorocarbon for this process. [For $\text{C}_2\text{Cl}_2\text{F}_2$, $C_p = 80.7 \text{ J mol}^{-1}\text{K}^{-1}$].

SOLUTIONS

1. (b) : $C_p = \frac{H_2 - H_1}{\Delta T} = \frac{\Delta H}{0} = \infty$ (infinity)

[$\Delta T = 0$ because two states (liquid and solid) of water are in equilibrium]

2. (c) : The enthalpy change depends on the initial and the final states and not on the path followed by the reaction.

3. (d) : $\frac{500 \text{ mL}}{0.5 \text{ h}} = \frac{M_{\text{SO}_2}}{M_{\text{He}}} = \sqrt{\frac{64}{4}} = 4$

$t = 4 \text{ h}$

4. (a) : $q_p - q_v = \Delta n_g RT$

($\Delta n = 12 - 15 = -3$)

$= -3 \times 8.314 \times 10^{-3} \times 298 = -7.43 \text{ kJ}$

5. (a) : Kinetic energy, $E = \frac{1}{2} Mu^2$

So, $u = \left(\frac{2E}{M}\right)^{1/2}$

6. (b) : Compressibility factor, $Z = \frac{(V)_{\text{obs}}}{(V)_{\text{ideal}}}$
 Given, $Z < 1$

$\therefore V_{\text{obs}} < V_{\text{ideal}}$ or $V_m < 22.4 \text{ L}$

7. (b)

8. (d) : It does not violate first law of thermodynamics but violates second law of thermodynamics.

9. (c) : van der Waals' equation for 1 mole of real gas is as follows :

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

But $b = 0$ (given)

$$\therefore \left(P + \frac{a}{V^2}\right)V = RT \text{ or } PV = -a \frac{1}{V} + RT \quad \dots(i)$$

$$(y = mx + c)$$

$$\therefore \text{Slope} = a = \frac{21.6 - 20.1}{3 - 2} = 1.5$$

10. (b) : In an ideal gas, there is no forces of attraction among the molecules. Therefore, $T_f = T_i$ for both reversible and irreversible expansions.

11. $u_{\text{rms}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times 8.314 \times 10^7 \times 293}{48}}$
 $= 3.9 \times 10^4 \text{ cm sec}^{-1}$

12. In an ideal gas, there exists no forces of attraction between the molecules. Hence, no energy is needed to overcome these forces. Also, when an ideal gas expands in vacuum ($P_{\text{ext}} = 0$), work done is zero.

13. The white cloud like trail that we see coming out of the high flying jet is water vapour issuing from the exhaust of high flying jets, getting converted directly into microcrystalline ice which is slowly reconverted into water vapour without passing through the liquid state.

14. Entropy decreases during the reaction as the number of particles on product side decreases. Hence, the sign of ΔS° will be negative.

15. (i) Height of a hill and (iii) Energy consumed in climbing the hill, are state functions.

16. True. The first law of thermodynamics deals with the equivalence of heat and work. The direction of a process is predicted by the second law of thermodynamics.

17. This is true under similar conditions of temperature and pressure. (According to Avogadro's law)

18. Boyle's temperature (T_B) = $\frac{a}{bR}$

\therefore Boyle's temperature for CO_2

$$= \frac{3.59 \text{ L}^2 \text{ atm mol}^{-2}}{(0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1})(0.0427 \text{ L mol}^{-1})} = 1024 \text{ K}$$

19. Since the standard enthalpy of formation of $\text{NO}_{(\text{g})}$ is positive, NO is thermodynamically unstable. From the given data, NO_2 is more stable than NO .

20. $\Delta_f H^\circ$ for $\text{Cl}_{2(\text{g})}$ is zero but $\Delta_f H^\circ$ for $\text{Br}_{2(\text{g})}$ will not be zero because the normal state of existence of bromine is liquid state not the gaseous state.



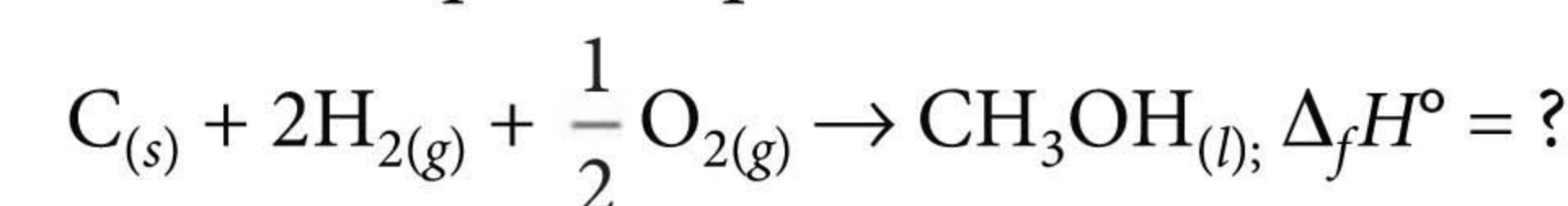
$\therefore 2 \text{ mol Al} = 3 \text{ mol H}_2$

$n_{\text{H}_2} \text{ released} = \frac{0.15 \text{ g}}{27 \text{ g mol}^{-1}} \times \frac{3}{2} = 8.33 \times 10^{-3} \text{ mol}$

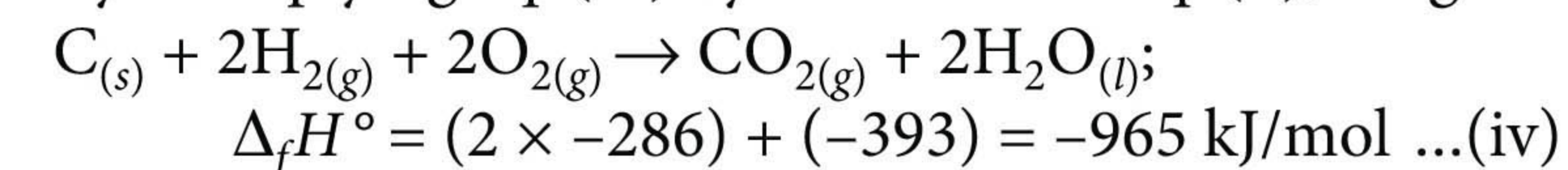
$V_{\text{H}_2} = \frac{n_{\text{H}_2} RT}{P}$
 $= \frac{8.33 \times 10^{-3} \text{ mol} \times 0.083 \text{ L bar mol}^{-1} \text{ K}^{-1} \times 293 \text{ K}}{1 \text{ bar}}$
 $= 0.203 \text{ L}$

$\therefore V_{\text{H}_2} = 203 \text{ mL}$

22. The required equation is

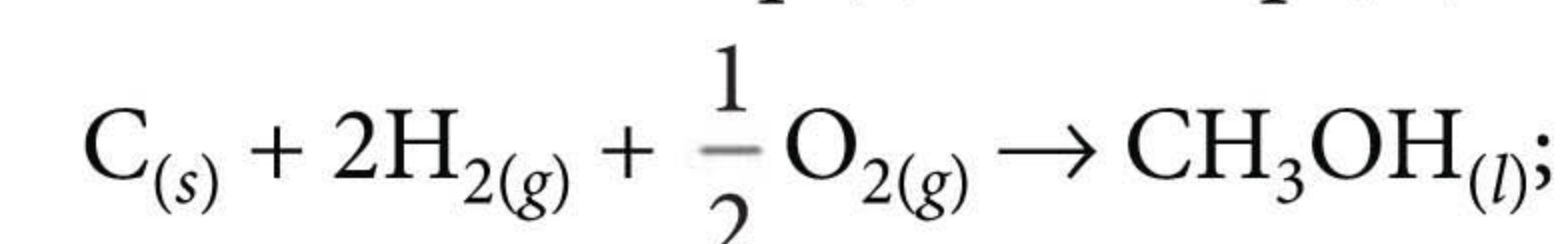


By multiplying eq. (iii) by 2 and add to eq. (ii), we get



$\Delta H = -572 - 393 = -965 \text{ kJ/mol}$

Now, subtract eq. (i) from eq. (iv), we get



$\Delta H = -965 - (-726) = -239 \text{ kJ/mol}$

23. In case heat is absorbed at constant pressure, we have
 $q_p = \Delta E - W = \Delta E + P\Delta V$ [$\because W = -P\Delta V$]
 $= (E_2 - E_1) + P(V_2 - V_1) = (E_2 + PV_2) - (E_1 + PV_1)$
 $= H_2 - H_1 = \Delta H$ [$\because H = E + PV$]

OR

$\Delta_{\text{vap}} H^\circ(\text{benzene}) = 30.8 \text{ kJ mol}^{-1}$

Molar mass of benzene, $\text{C}_6\text{H}_6 = (6 \times 12 + 6 \times 1) \text{ g mol}^{-1}$
 $= 78 \text{ g mol}^{-1}$

Energy needed to vaporise benzene

$= 30.8 \text{ kJ mol}^{-1} \times \frac{100 \text{ g}}{78 \text{ g mol}^{-1}} = 39.49 \text{ kJ}$

So, Time = $\frac{\text{Energy}}{\text{Power}} = \frac{39.49 \text{ kJ}}{100 \text{ W}} = \frac{39.49 \times 10^3 \text{ J}}{100 \text{ J s}^{-1}}$
 $= 394.9 \text{ s} = 6.6 \text{ min}$

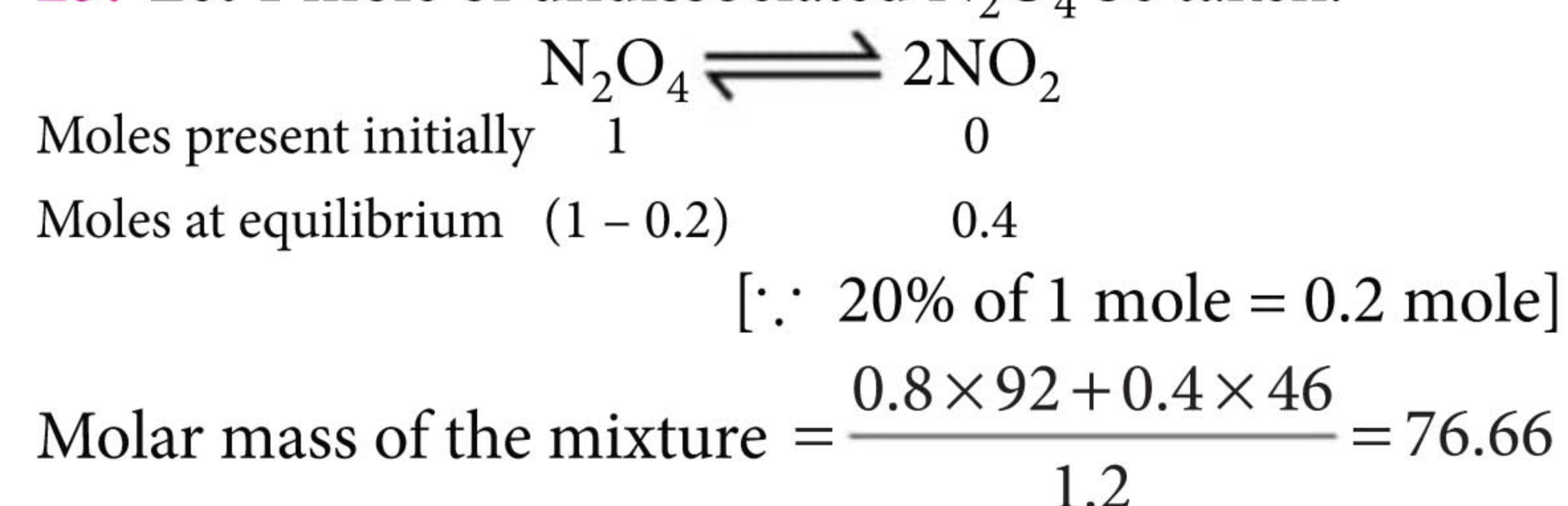
24. From the ideal gas equation, $PV = nRT$

$PV = \frac{m}{M} RT \Rightarrow P = \frac{m}{V} \times \frac{RT}{M} = d \frac{RT}{M} \therefore d = \frac{MP}{RT}$

Substituting the values, we get

$d = \frac{17 \times 5}{0.0821 \times 303} = 3.42 \text{ g/litre}$

25. Let 1 mole of undissociated N_2O_4 be taken.



$$\text{Now, } d = \frac{PM}{RT} = \frac{1 \times 76.66}{0.0821 \times 300} = 3.112 \text{ g L}^{-1}$$

26. In general, those compounds which are formed by absorption of heat are less stable than those formed with release of heat because less the energy, more stable is compound.

Hence, increasing stability of the given compounds is in the order :



OR

(a) Energy needed = $m \times c \times \Delta t$
 $= 10.0 \times 0.45 \times (500 - 25) = 2137.5 \text{ J}$

(b) The reaction would be always spontaneous when both energy factor and randomness factor favour it, i.e., $\Delta H = -\text{ve}$ and $\Delta S = +\text{ve}$

27. (i) Higher the critical temperature more easily the gas can be liquefied and stronger are the intermolecular forces. Therefore, CO_2 has stronger intermolecular forces than CH_4 .

(ii) 'a' is a measure of the magnitude of the intermolecular forces of attraction while 'b' is a measure of the effective size of the gas molecules.

28. The overall process is a cyclic one as the initial state is regained.

$$\text{Total work, } w = w_{a \rightarrow b} + w_{b \rightarrow c} + w_{c \rightarrow a}$$

$$w_{a \rightarrow b} = -P \times (V_2 - V_1) = -1 \times (40 - 20) = -20 \text{ L atm}$$

$$w_{b \rightarrow c} = -P \times (V_2 - V_1) = -1 \times 0 = 0$$

$$w_{c \rightarrow a} = +2.303nRT \log \frac{V_2}{V_1} \quad (\text{Work of compression})$$

$$= +2.303 \times 1 \times 20 \log \frac{40}{20} = 13.86$$

$$\therefore \text{Total work (w)} = -20 + 13.86 = -6.14 \text{ L atm}$$

$$= -6.14 \times 101.3 \text{ J} = -621.98 \text{ J}$$

$$q = -w = +621.98 \text{ J}$$

As the process is cyclic, therefore $\Delta U = 0$

$$29. P_1 = 700 \text{ mm, } P_2 = 760 \text{ mm}$$

$$V_1 = 1336 \text{ mL, } V_2 = ?, T_1 = 300 \text{ K, } T_2 = 273 \text{ K}$$

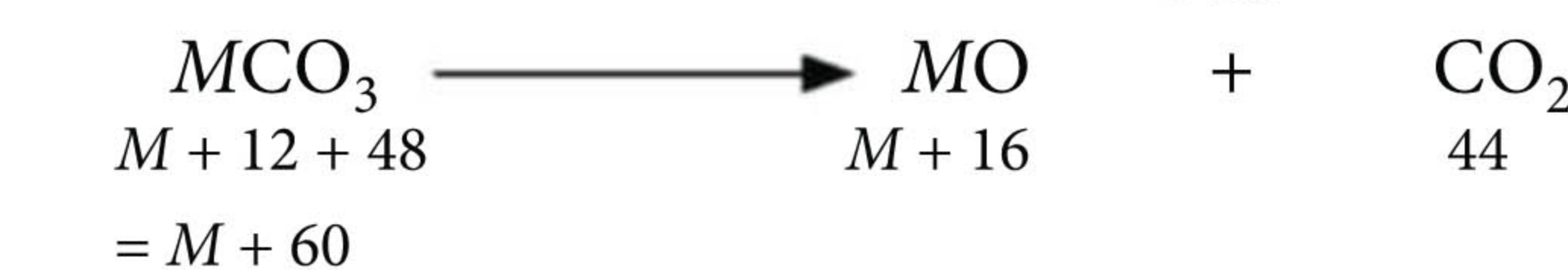
$$\text{Since } \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$\therefore V_2 = \frac{700 \times 1336 \times 273}{300 \times 760} = 1.12 \text{ L at N.T.P.}$$

$$1.12 \text{ L CO}_2 \text{ is given by carbonate} = 4.215 \text{ g}$$

$$22.4 \text{ L CO}_2 \text{ is given by carbonate} = \frac{4.215}{1.12} \times 22.4 \text{ g}$$

$$= 84.3$$



As, molecular weight of carbonate = 84.3

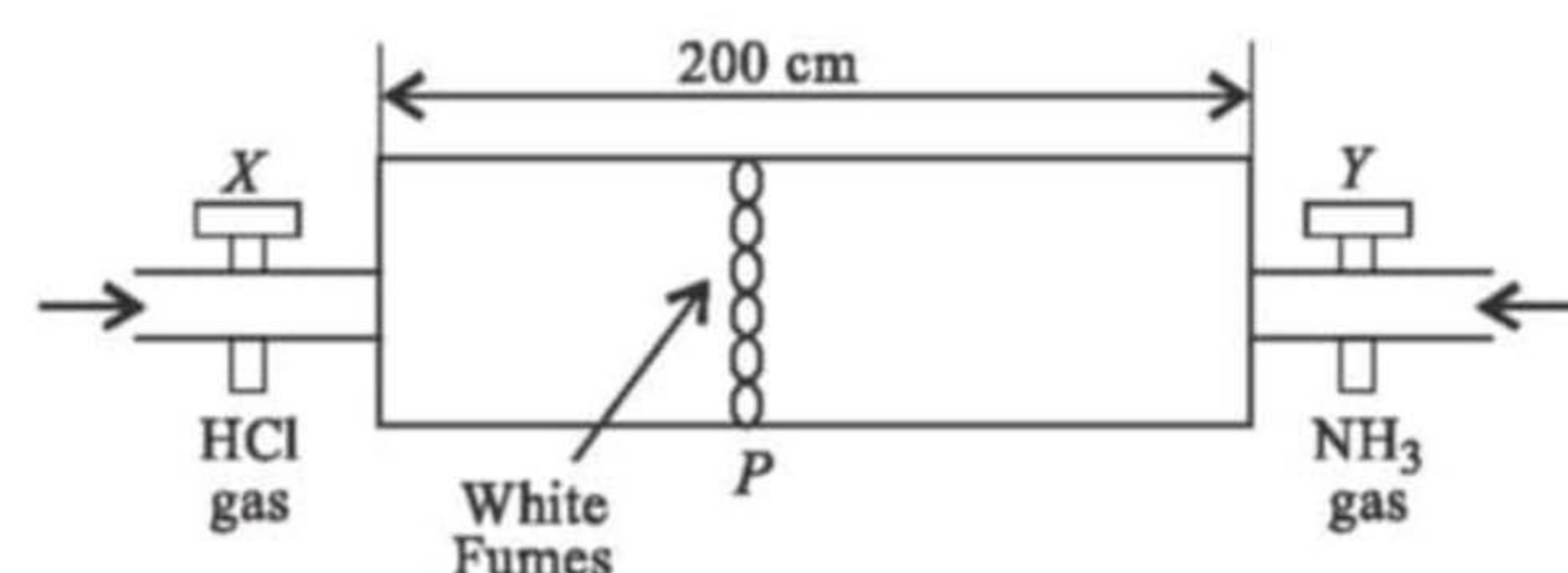
$$\therefore \text{Atomic weight of } M = 84.3 - 60 = 24.3$$

$$\therefore \text{Equivalent weight of } M = \frac{1}{2} \times 24.3 = 12.15$$

OR

Let ammonia diffuses through = x cm.

and HCl diffuses through = y cm.



Molecular weight of $\text{NH}_3 = 17$

Molecular weight of $\text{HCl} = 35.5 + 1 = 36.5$

According to the Graham's law of diffusion

$$\frac{x}{y} = \sqrt{\frac{36.5}{17}} = \sqrt{2.147} = 1.465$$

$$\therefore \frac{x}{y} = 1.465 \text{ or } x = 1.465y$$

$$x + y = 200 \text{ cm}$$

$$1.465y + y = 200 \text{ or } y(1.465 + 1) = 200 \text{ cm}$$

$$\therefore y = \frac{200}{2.465} = 81.13 \text{ cm}$$

Distance between P and X = 81.13 cm

30. Case I : Let molar weight of gas be $M \text{ g mol}^{-1}$

Weight of gas = 2.9 g

$$\text{No. of moles} = \frac{\text{Weight}}{\text{Molar weight}} = \frac{2.9}{M}$$

$$T = 273 + 95 = 368 \text{ K}$$

$$PV = \frac{2.9}{M} \times R \times 368 \quad \dots(i)$$

Case II : Mass of dihydrogen = 0.184 g

$$\text{No. of moles of H}_2 = \frac{0.184}{2}$$

$$T = 273 + 17 = 290 \text{ K}$$

$$PV = \frac{0.184}{2} \times R \times 290 \quad \dots(ii)$$

From equations (i) and (ii),

$$\frac{2.9}{M} \times 368 = \frac{0.184}{2} \times 290$$

$$M = \frac{2.9 \times 368 \times 2}{0.184 \times 290} = 40 \text{ g mol}^{-1}$$

31. (i) The extent to which a real gas deviates from ideal behaviour can be conveniently studied in terms of quantity 'Z' called the compressibility factor, which is defined as $Z = \frac{PV}{nRT}$

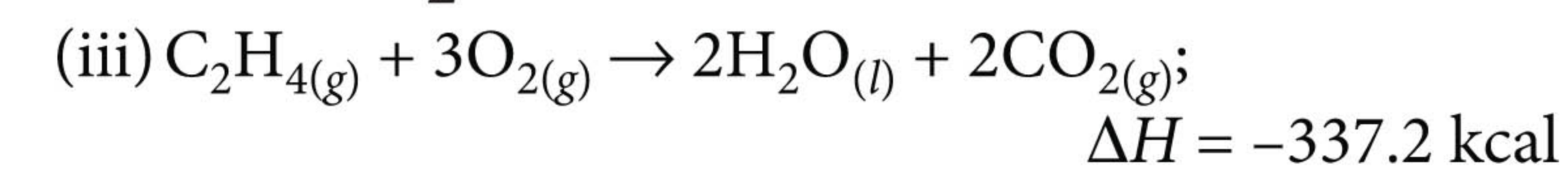
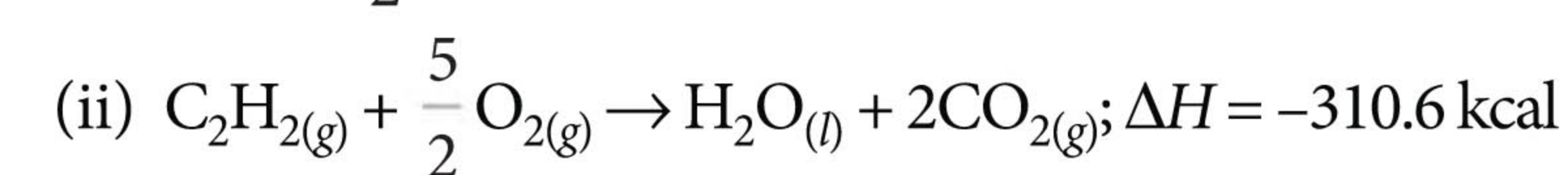
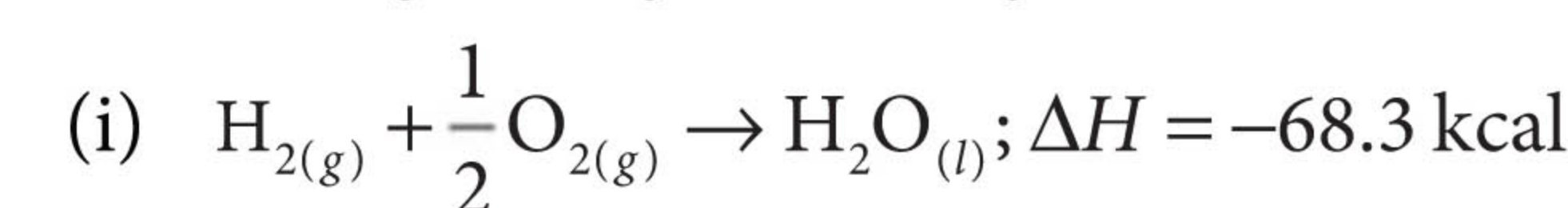
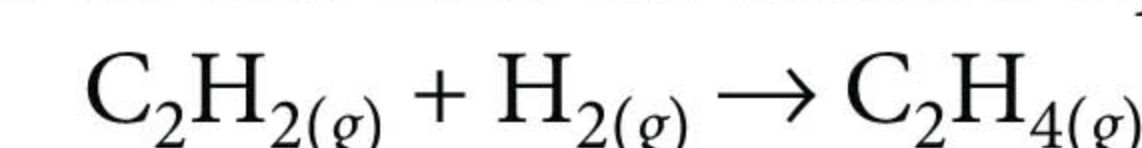
For an ideal gas, as $PV = nRT$, $Z = 1$

(ii) For an ideal gas, $Z = 1$

For a non-ideal (real) gas, $Z \neq 1$, either $Z > 1$ or $Z < 1$

(iii) Above Boyle's temperature value of Z is greater than one.

32. In this case the desired equation is



To get the desired equation add (i) and (ii) and subtract (iii), then

$$\Delta H = -68.3 + (-310.6) - (-337.2) \text{ kcal}$$

$$\text{or } \Delta H = -41.7 \text{ kcal}$$

$$\Delta H = \Delta U + \Delta n_g RT$$

$$\therefore \Delta U = \Delta H - \Delta n_g RT$$

$$= -41.7 - (-1 \times 2 \times 10^{-3} \times 298) \text{ kcal}$$

$$= (-41.7 + 0.596) \text{ kcal} \quad [\because R = 2 \times 10^{-3} \text{ kcal/K/mole}]$$

$$= -41.104 \text{ kcal}$$

OR

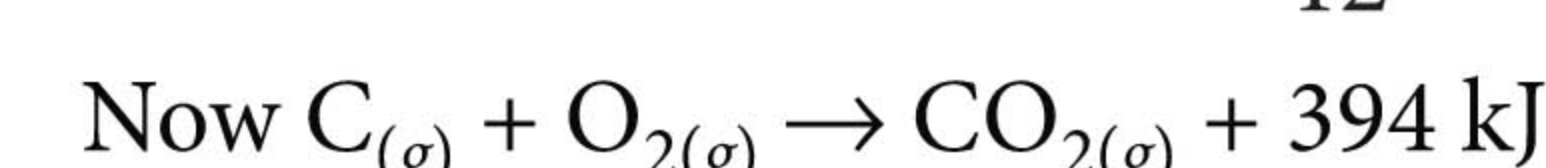
$$\text{Wt. of pure coal} = \frac{80}{100} \times 10 = 8.0 \text{ kg}$$

$$\text{Wt. of coal converted into CO}_2 = 8 \times \frac{60}{100} = 4.8 \text{ kg}$$

$$\text{Wt. of coal converted into CO} = 8 - 4.8 = 3.2 \text{ kg}$$

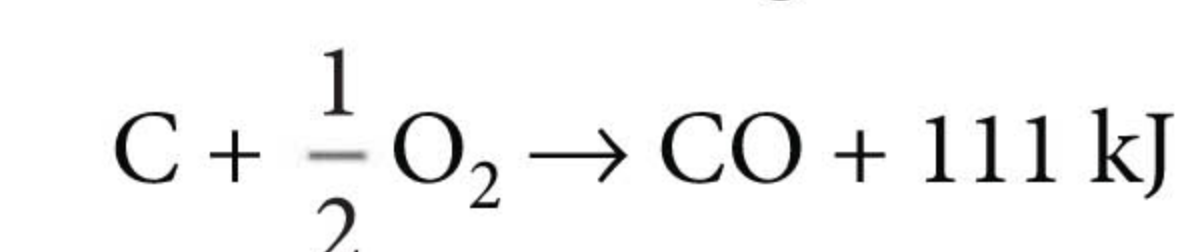
$$\text{Moles of C in 4.8 kg coal} = \frac{4800}{12} = 400 \text{ moles}$$

$$\text{Moles of C in 3.2 kg coal} = \frac{3200}{12} = 266.67 \text{ moles}$$



1 mole of C gives heat = 394 kJ

$$\therefore 400 \text{ moles of C give heat} = 400 \times 394 = 157600 \text{ kJ}$$



1 mole of C gives heat = 111 kJ

$$\therefore 266.67 \text{ moles of C gives heat} = 111 \times 266.67 = 29600 \text{ kJ}$$

$$\text{Total heat generated} = 157600 + 29600 = 187200 \text{ kJ}$$

33. (a) According to Charles' law.

$$V_t = V_0 \left[1 + \frac{t}{273} \right]$$

At, $t = -273^\circ\text{C}$

$$V_t = V_0 \left[1 - \frac{273}{273} \right] = 0$$

Thus, -273°C is the lowest temperature because below this temperature, the volume will become negative which is meaningless.

(b) Pressure at the surface = 76 cm of Hg

$$= 76 \times 13.6 \text{ cm of H}_2\text{O} = 10.3 \text{ m of H}_2\text{O}$$

$$\therefore \text{Pressure at 100 m depth}$$

$$= 100 + 10.3 \text{ m} = 110.3 \text{ m}$$

Applying

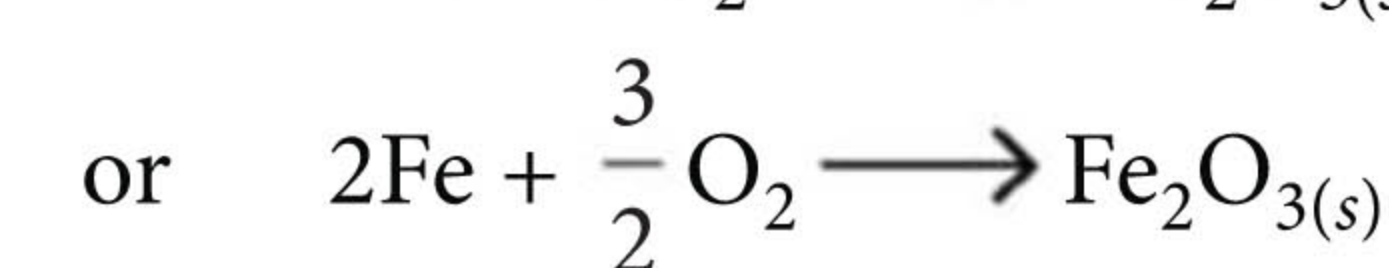
$$P_1 V_1 = P_2 V_2,$$

(At surface) (At 100 m depth)

$$10.3 \times V = 110.3 \times V_2$$

$$\text{or } V_2 = 0.093 V = 9.3 \% \text{ of } V$$

34. (a) The formation of ferric oxide may be written as,



$$(2 \times 56) = 112 \text{ g} \quad 1 \text{ mol}$$

Thus, to obtain one mole of Fe_2O_3 , 112 g of iron is required. Therefore,

Energy produced by burning 60 g of Fe = 43.9 kJ

$$\text{Energy produced by burning 112 g of Fe} = 112 \times \frac{43.9}{60} \text{ kJ}$$

$$= 81.9 \text{ kJ}$$

Thus, 81.9 kJ of energy is obtained when 1 mole of ferric oxide is obtained from iron and oxygen. Thus, the enthalpy of formation ($\Delta_f H$) of $\text{Fe}_2\text{O}_{3(s)}$ is $-81.9 \text{ kJ mol}^{-1}$.

(b) We know,

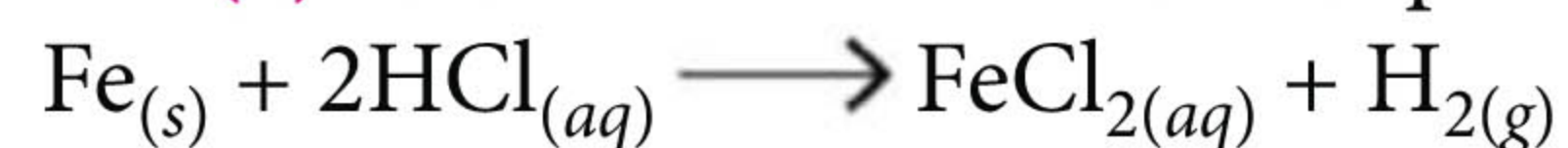
$$\Delta U = \Delta H - (\Delta n)_g RT$$

$$\text{Here, } (\Delta n)_g = 2 - (1 + 3) = -2$$

$$\text{So, } \Delta U = -92.38 - 2 \times 8.314 \times 10^{-3} \times 298$$

$$\text{or } \Delta U = -92.38 \text{ kJ mol}^{-1} - 4.96 \text{ kJ mol}^{-1} = -97.34 \text{ kJ mol}^{-1}$$

35. (a) Iron reacts with HCl and produces H₂ gas.



Thus, 1 mol of Fe produces 1 mole of H₂ gas

$$\therefore 11.2 \text{ g Fe will produce} = \frac{1 \times 11.2}{56} = 0.2 \text{ mol of H}_2$$

(i) If the reaction is carried out in a closed vessel, then $\Delta V = 0$ $\therefore w = -P_{\text{ext}}\Delta V = 0$

(ii) If the reaction is carried out in an open vessel with external pressures being 1 atm, then

Initial volume = 0 (because no gas is present)

Final volume = 0.2 mol of H₂ at 25°C and 1 atm pressure

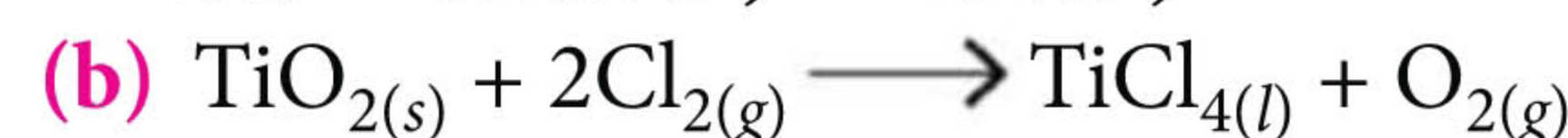
Now, $PV = nRT$

$$\therefore V = \frac{nRT}{P} = \frac{0.2 \times 0.0821 \times 298}{1} = 4.89 \text{ L}$$

$$\therefore \text{Change in volume, } \Delta V = V_{\text{final}} - V_{\text{initial}} = 4.89 \text{ L}$$

$$w = -P_{\text{ext}}\Delta V = -1 \text{ atm} \times 4.89 \text{ L} = -4.89 \text{ L atm}$$

$$= -4.89 \times 101.325 \text{ J} = -495.5 \text{ J}$$



$$\Delta H_{\text{reaction}}^{\circ} = [H_{\text{TiCl}_{4(l)}}^{\circ} + H_{\text{O}_{2(g)}}^{\circ}] - [H_{\text{TiO}_{2(s)}}^{\circ} + 2 \times H_{\text{Cl}_{2(g)}}^{\circ}]$$

$$= [-804.2 + 0.0] - [-944.7 + 0.0] = 140.5 \text{ kJ mol}^{-1}$$

$$\text{Also, } \Delta S_{\text{reaction}}^{\circ} = [S_{\text{TiCl}_{4(l)}}^{\circ} + S_{\text{O}_{2(g)}}^{\circ}] - [S_{\text{TiO}_{2(s)}}^{\circ} + 2 \times S_{\text{Cl}_{2(g)}}^{\circ}]$$

$$= [252.3 + 205.1] - [50.3 + 2 \times 233.0] = -58.9 \text{ J}$$

$$= -0.0589 \text{ kJ}$$

$$\text{Now, } \Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$$

$$= 140.5 - 298.15 \times (-0.0589) = 158.06 \text{ kJ}$$

As ΔG° for the reaction is positive, the above reaction is not possible.

OR

$$\text{(a) (1) } \Delta G = \Delta H - T\Delta S \Rightarrow +1.193 = 41.1 - 363 \times \Delta S$$

$$363 \times \Delta S = 41.1 - 1.193 = 39.907$$

$$\therefore \Delta S = \frac{39.907}{363} = 0.1099 \text{ kJ mol}^{-1} \text{ K}^{-1}$$

$$\therefore = 110 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$(2) T\Delta S = 373.3 \times 109 = 40689.7 = 40.69 \text{ kJ mol}^{-1}$$

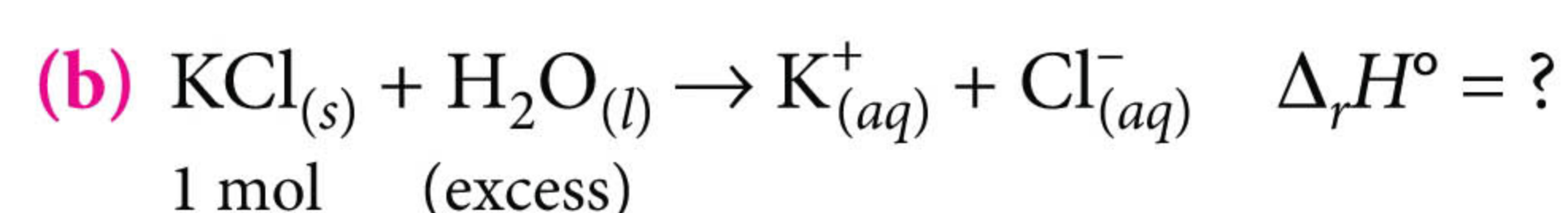
$$\Delta G = \Delta H - T\Delta S = 40.7 - 40.69$$

$$\therefore = -0.01 \text{ kJ mol}^{-1}$$

$$(3) \Delta G = \Delta H - T\Delta S \Rightarrow -0.979 = 40.1 - T\Delta S$$

$$\therefore T\Delta S = 40.1 + 0.979 = 41.079 \text{ kJ mol}^{-1}$$

$$\Delta S = \frac{41.079}{383} = 0.1072 \text{ kJ mol}^{-1} \text{ K}^{-1} = 107.2 \text{ J mol}^{-1} \text{ K}^{-1}$$



$$\Delta_r H^{\circ} = [\Delta_f H^{\circ}(\text{K}_{(aq)}^{+}) + \Delta_f H^{\circ}(\text{Cl}_{(aq)}^{-})] - [\Delta_f H^{\circ}(\text{KCl})]$$

$$= [-251.2 + (-167.08)] \text{ kJ mol}^{-1} - [-437.6 \text{ kJ mol}^{-1}]$$

$$= -418.28 \text{ kJ mol}^{-1} + 437.6 \text{ kJ mol}^{-1}$$

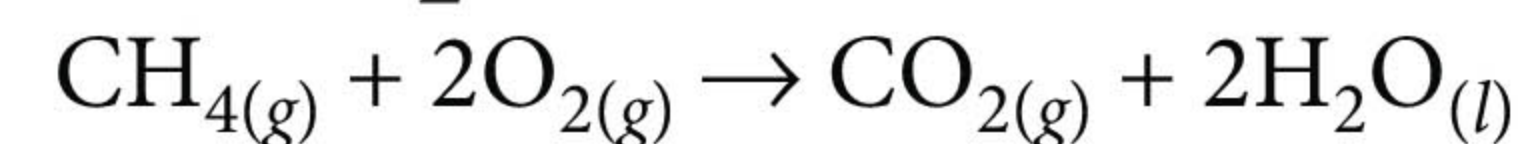
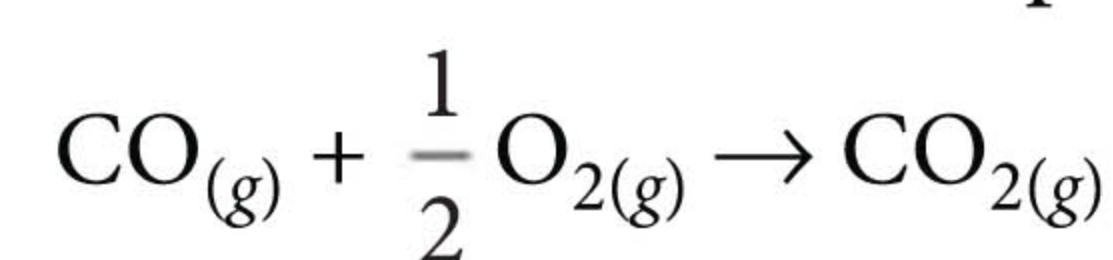
$$\Delta_r H^{\circ} = +19.3 \text{ kJ mol}^{-1}$$

This process does not represent an ionisation reaction.

The process here involves dissolution of KCl_(s) in water and formation of K_(aq)⁺ and Cl_(aq)⁻ by dissociation.

36. Under given conditions CO_(g) and CH_{4(g)} react with oxygen to form CO_{2(g)} and H₂O_(l) but helium remains unaffected.

The reactions can be represented as:



Let the volume of CO_(g) and CH_{4(g)} in the gaseous mixture be x and y mL respectively. Then volume of He in the gaseous mixture = $[20 - (x + y)]$ mL

After the reaction, the mixture consists of CO_{2(g)} formed by the action of O₂ on CO and CH₄ and helium (He) that remains as such.

$$\text{Volume of left hand side in the above reactions} - 13$$

$$= \text{Volume of right hand side}$$

$$\text{or } [20 - (x + y)] + \left(x + \frac{1}{2}x\right) + (y + 2y) - 13$$

$$= [20 - (x + y)] + (x + y)$$

$$[\because \text{For gases, volume} \propto \text{number of moles}]$$

$$\text{or } \frac{1}{2}x + 2y = 13 \text{ or } x + 4y = 26 \quad \dots(i)$$

The volume of CO_{2(g)} formed in the above reaction is x mL from x mL of CO_(g) and y mL from y mL of CH_{4(g)} i.e. total volume of CO_{2(g)} formed is $(x + y)$ mL

$$\therefore x + y = 14 \text{ mL} \quad \dots(ii)$$

[KOH absorbs CO₂ when gaseous mixture is passed through it to form K₂CO₃ and H₂O]

From (i) and (ii),

$$3y = 12 \text{ or } y = 4 \text{ mL and } x = 14 - 4 = 10 \text{ mL}$$

$$\therefore \text{Volume of CO in mixture} = 10 \text{ mL}$$

$$\text{Volume of CH}_4 \text{ in mixture} = 4 \text{ mL}$$

$$\text{Volume of He in mixture} = 20 - (10 + 4) = 6 \text{ mL}$$

$$\text{Hence \% of CO} = \frac{10}{20} \times 100 = 50\%$$

$$\% \text{ of CH}_4 = \frac{4}{20} \times 100 = 20\%$$

$$\% \text{ of He} = \frac{6}{20} \times 100 = 30\%$$

OR

(a) Suppose molecular masses of A and B are M_A and M_B respectively. Then their number of moles will be

$$n_A = \frac{1}{M_A}, n_B = \frac{2}{M_B}$$

$$P_A = 2 \text{ bar, } P_A + P_B = 3 \text{ bar} \Rightarrow P_B = 1 \text{ bar}$$

$$\text{Applying the } PV = nRT$$

$$P_A V = n_A RT, P_B V = n_B RT$$

$$\frac{P_A}{P_B} = \frac{n_A}{n_B} = \frac{1/M_A}{2/M_B} = \frac{M_B}{2M_A}$$

$$\frac{M_B}{M_A} = 2 \times \frac{P_A}{P_B} = 2 \times \frac{2}{1} = 4$$

$$\therefore M_B = 4M_A$$

(b) Mass of LPG originally present

$$= 29.0 - 14.8 = 14.2 \text{ kg}$$

Original pressure = 2.5 atm

Mass of LPG present after use = 23.2 - 14.8 = 8.4 kg

Since the volume of the cylinder is constant, hence

$$\frac{P_1}{P_2} = \frac{n_1}{n_2} = \frac{w_1/M}{w_2/M} = \frac{w_1}{w_2} \text{ or } \frac{2.5}{P_2} = \frac{14.2}{8.4}$$

$$\therefore P_2 = \frac{2.5 \times 8.4}{14.2} = 1.48 \text{ atm}$$

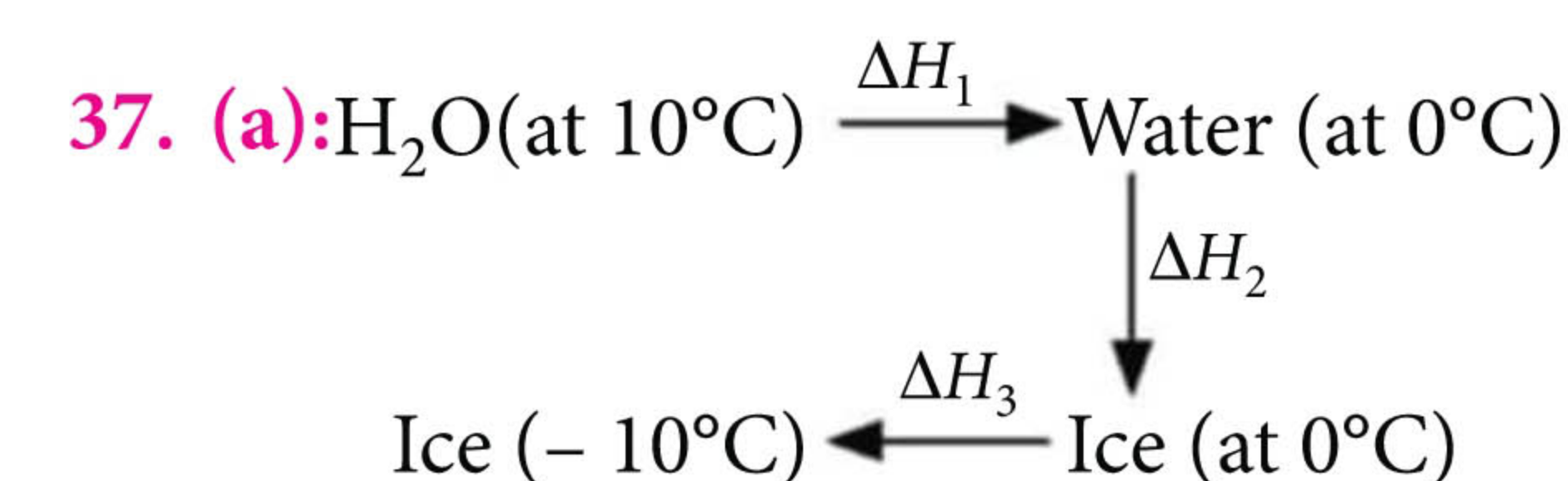
Mass of LPG used = 14.2 - 8.4 = 5.8 kg

$$\text{Moles of } n\text{-butane} = \frac{5.8 \times 1000}{58} = 100 \text{ moles}$$

Again, $PV = nRT$

Volume of 100 moles of LPG at 1 atm pressure and 300 K temperature,

$$= 2463 \text{ litres} = 2.463 \text{ m}^3$$



$$\Delta H_1 = C_p(\text{H}_2\text{O}_{(l)}) \times \Delta T = 75.3 \text{ J mol}^{-1} \text{ K}^{-1} \times (-10^\circ\text{C})$$

$$= -753 \text{ J mol}^{-1} = -0.753 \text{ kJ mol}^{-1}$$

$$\Delta H_2 = \Delta_{\text{fus}} H = -6.03 \text{ kJ mol}^{-1}$$

$$\Delta H_3 = C_p(\text{H}_2\text{O}_{(s)}) \times \Delta T = 36.8 \text{ J mol}^{-1} \text{ K}^{-1} \times (-10^\circ\text{C})$$

$$= -368 \text{ J mol}^{-1} = -0.368 \text{ kJ mol}^{-1}$$

Total enthalpy change

$$= -0.735 \text{ kJ mol}^{-1} - 6.03 \text{ kJ mol}^{-1} - 0.368 \text{ kJ mol}^{-1}$$

$$= -7.133 \text{ kJ mol}^{-1}$$

(b) From the second equation,

$$\Delta_{\text{diss}} H^{\circ} = [\Delta_f H^{\circ}(\text{H}_3\text{O}^{+}) + \Delta_f H^{\circ}(\text{Cl}^{-})] - [\Delta_f H^{\circ}(\text{HCl}_{(g)})]$$

$$-75.2 \text{ kJ mol}^{-1} = [0 + \Delta_f H^{\circ}(\text{Cl}_{(aq)}^{-})] + 92.8 \text{ kJ mol}^{-1}$$

$$\text{So, } \Delta_f H^{\circ}(\text{Cl}_{(aq)}^{-}) = -75.2 \text{ kJ mol}^{-1} - 92.8 \text{ kJ mol}^{-1}$$

$$\text{or } \Delta_f H^{\circ}(\text{Cl}_{(aq)}^{-}) = -168.0 \text{ kJ mol}^{-1}$$

OR

(a) The part of the universe chosen for thermodynamic consideration, (i.e., to study the effect of temperature, pressure, etc.) is called a system. The remaining portion of the universe, excluding the system, is called surroundings.

Thus, system and surroundings together constitute the universe, i.e.,

Universe = System + Surrounding.

Adiabatic process : When a process is carried out in such a manner that no heat can flow from the system to the surrounding or vice versa, i.e., the system is completely insulated from the surrounding, it is called an adiabatic process.

(b) Mass of the gas = 1.25 g

Molar mass of the gas

$$= (2 \times 12 + 2 \times 35.5 + 2 \times 19) \text{ g mol}^{-1} = 133 \text{ g mol}^{-1}$$

$$\text{Mole of the gas} = 1.25 \text{ g} / 133 \text{ g mol}^{-1} = 9.4 \times 10^{-3} \text{ mol}$$

$$\text{Volume of gas at } 320 \text{ K} = 274 \text{ mL}$$

$$\text{Volume of gas at } 293 \text{ K} = 248 \text{ mL}$$

Molar heat capacity of the gas at constant P ,

$$C_p = 80.7 \text{ J mol}^{-1} \text{ K}^{-1}$$

For the adiabatic reversible expansion of gas,

$$\Delta H = n C_p (T_2 - T_1)$$

$$= 9.4 \times 10^{-3} \text{ mol} \times 80.7 \text{ J mol}^{-1} \text{ K}^{-1} \times (293 - 320) \text{ K}$$

$$\therefore \Delta H = -20.5 \text{ J}$$

$$\text{and } \Delta U = n C_v (T_2 - T_1) = n \times (C_p - R) (T_2 - T_1)$$

$$= 9.4 \times 10^{-3} (80.7 - 8.3) \text{ J K}^{-1} \text{ mol}^{-1} \times (293 - 320) \text{ K}$$

$$\therefore \Delta U = -18.4 \text{ J}$$



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HIGHLIGHTS

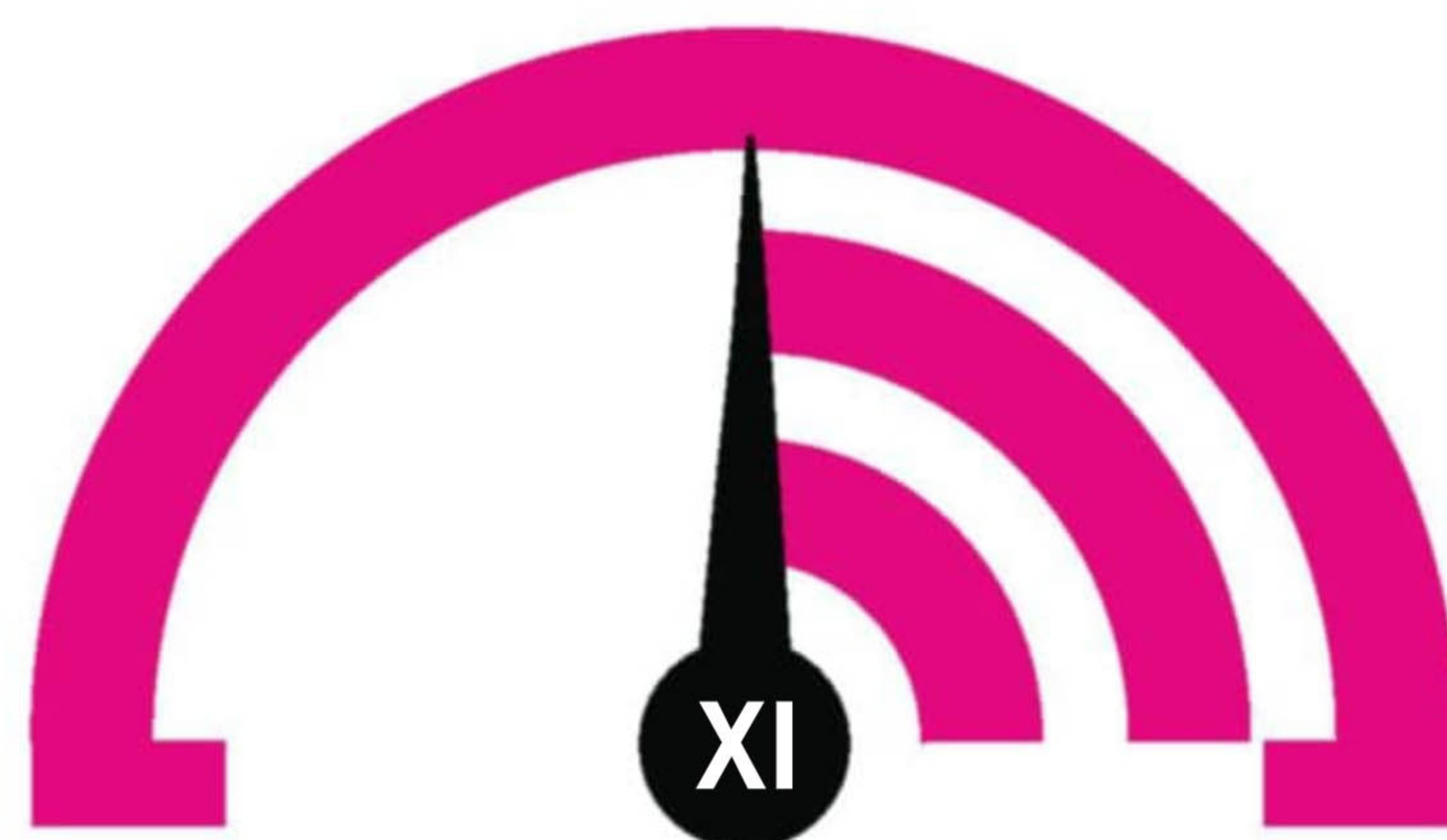
- Important Facts/Formulae & Comprehensive Theory
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MONTHLY TEST DRIVE



This specially designed column enables students to self analyse their extent of understanding of specified chapters. Give yourself four marks for correct answer and deduct one mark for wrong answer. Self check table given at the end will help you to check your readiness.

Total Marks : 120

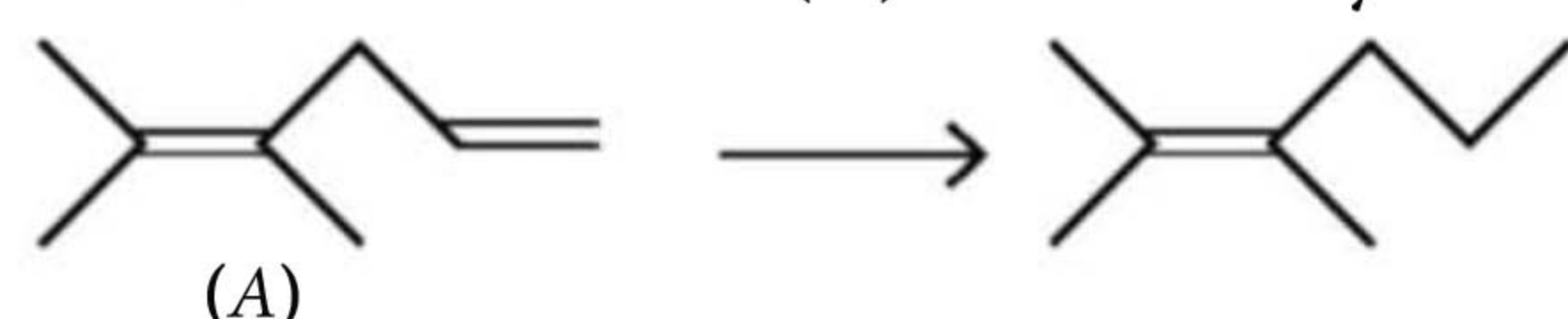
Hydrocarbons

Time Taken : 60 Min.

NEET / AIIMS

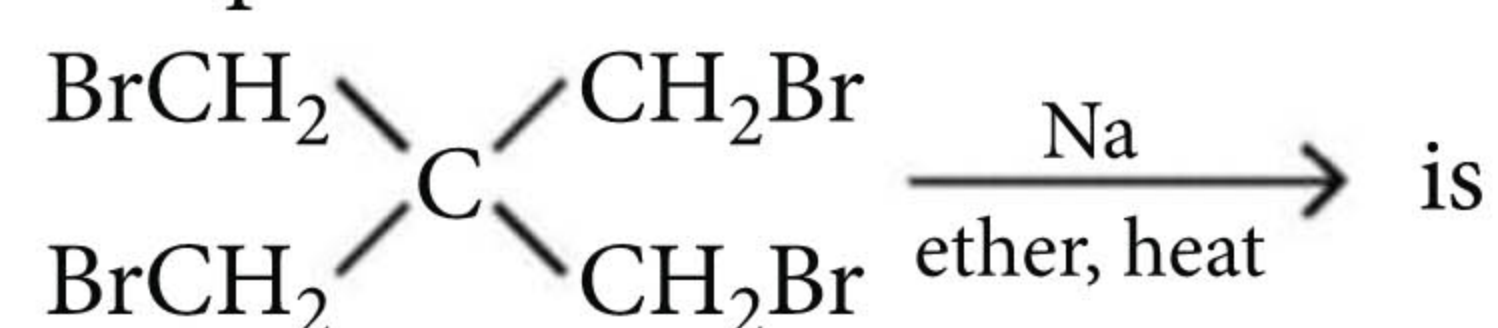
Only One Option Correct Type

1. Partial reduction of (A) is selectively done using



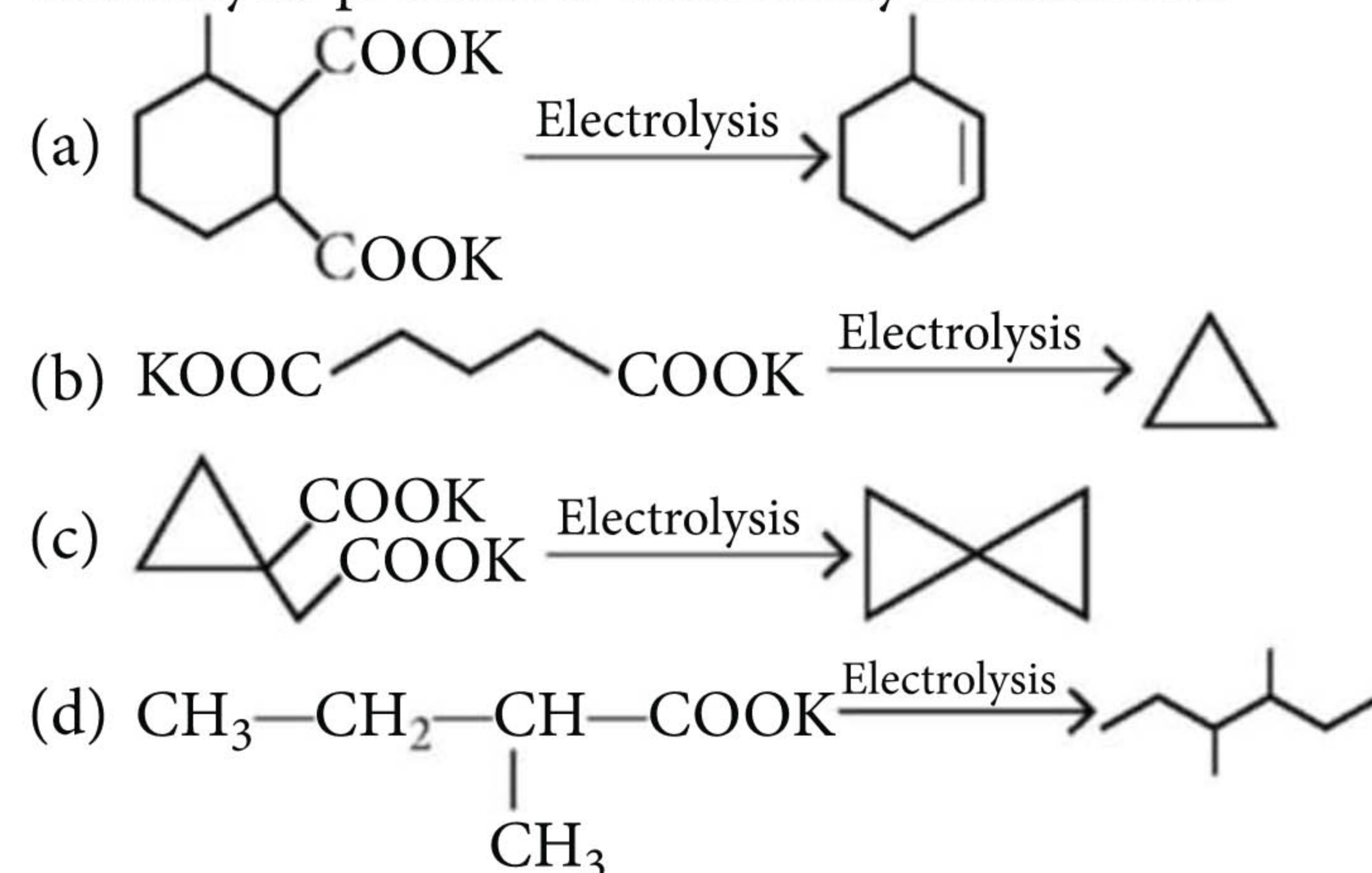
- (a) $\text{SiH}_2\text{BH}/\text{THF}$
(b) $\text{B}_2\text{H}_6/\text{H}_2\text{O}_2, \text{OH}^-$
(c) $\text{B}_2\text{H}_6/\text{AgNO}_3 - \text{NaOH}$
(d) NaBH_4

2. The product formed in the reaction,

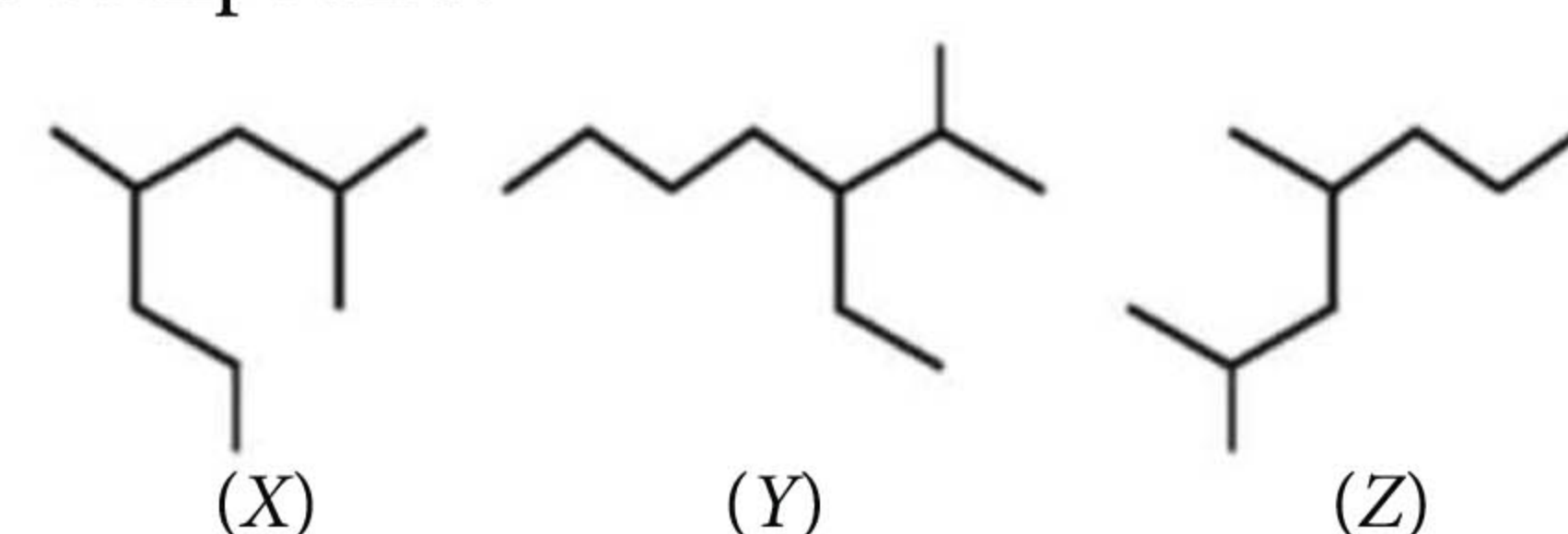


- (a) $(\text{BrCH}_2)_3\text{CCH}_2\text{CH}_2\text{C}(\text{CH}_2\text{Br})_3$
(b) $\text{BrCH}_2\text{C}(\text{CH}_2\text{Br})_2\text{CH}_2\text{Br}$
(c) $\text{BrCH}_2\text{C}(\text{CH}_2\text{Br})_3$
(d) C_2H_6

3. In which of the following reactions, the Kolbe's electrolysis product is incorrectly mentioned?

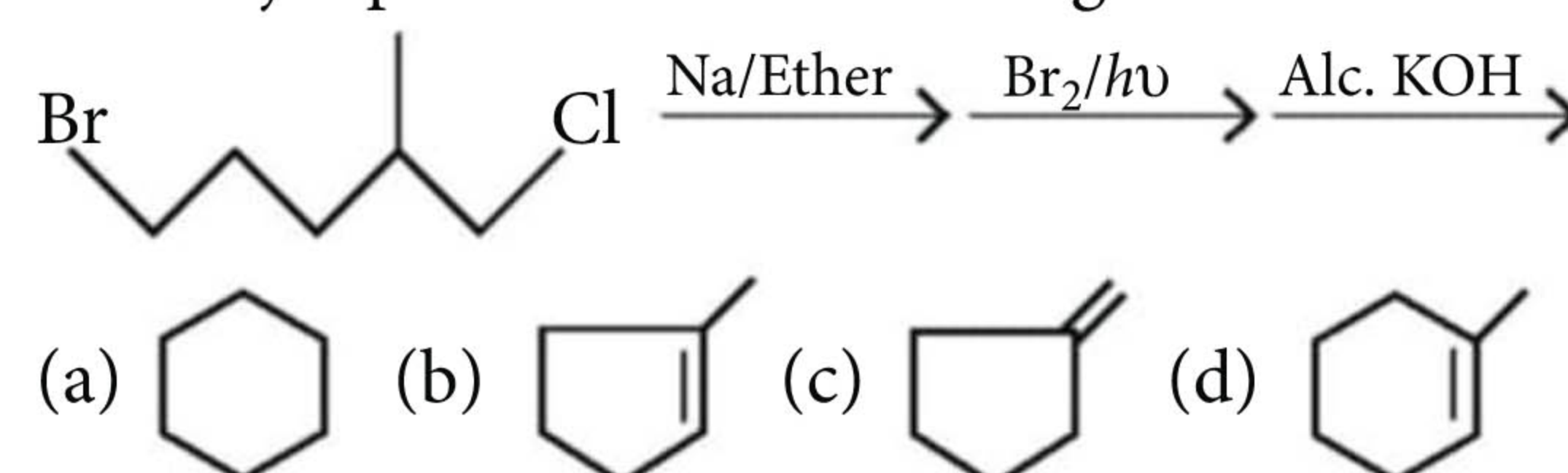


4. Out of the following which structures represent the same compound?



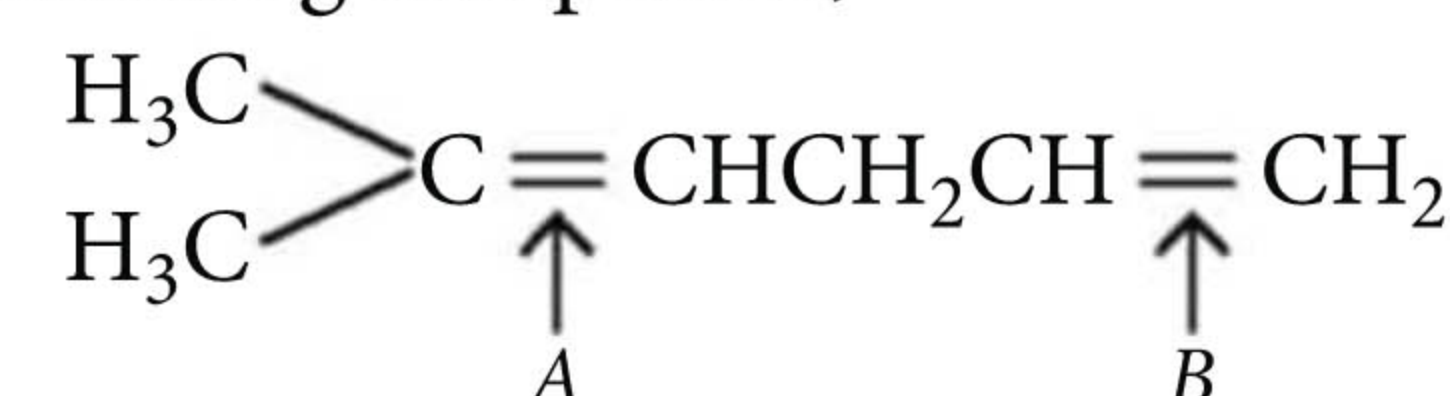
- (a) X, Z (b) X, Y
(c) Y, Z (d) X, Y, Z

5. The major product of the following reaction is



- (a) (b) (c) (d)

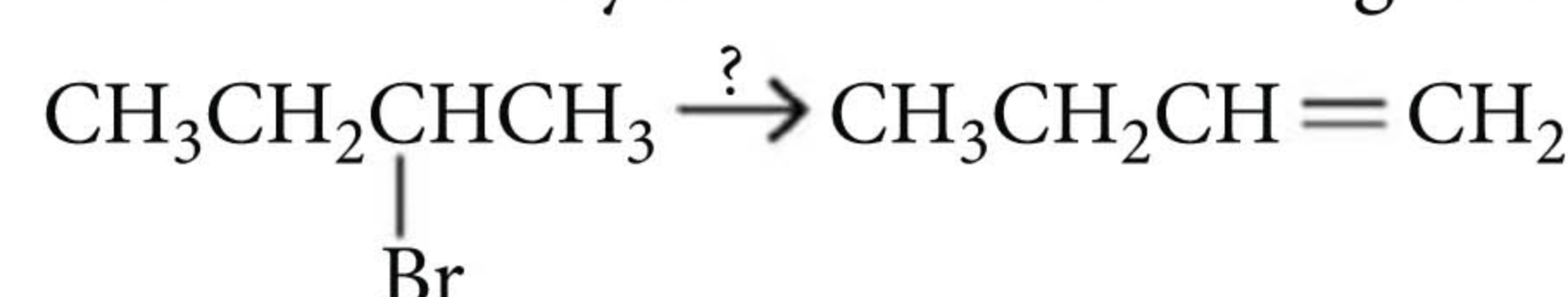
6. In the following compound,



which (C = C) bond is more nucleophilic?

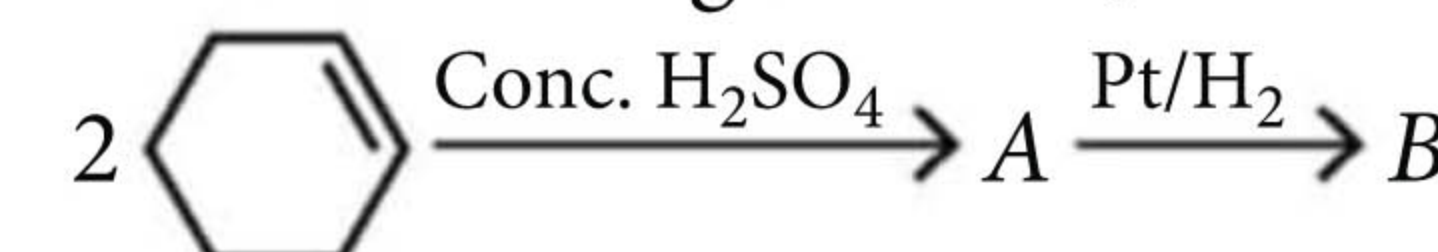
- (a) A
(b) B
(c) Equally nucleophilic
(d) C = C is not nucleophilic

7. Which conditions/reagents would you employ to obtain the best yields in the following reaction?



- (a) $\text{H}_2\text{O}/\text{heat}$
(b) $(\text{CH}_3)_3\text{COK}/(\text{CH}_3)_3\text{COH}, \text{heat}$
(c) $\text{CH}_3\text{CH}_2\text{ONa}/\text{CH}_3\text{CH}_2\text{OH}, \text{heat}$
(d) $\text{KOH}(\text{alc.})/\text{heat}$

8. In the following reaction,



A and B respectively are

- (a) both and
(b) and
(c) and
(d) and

9. 2-Hexyne changes to 1-hexyne by using
(a) $\text{NaNH}_2/\text{H}_2\text{O}$ (b) $\text{KOH}/\text{CH}_3\text{CH}_2\text{OH}$
(c) both (a) and (b) (d) none of these.

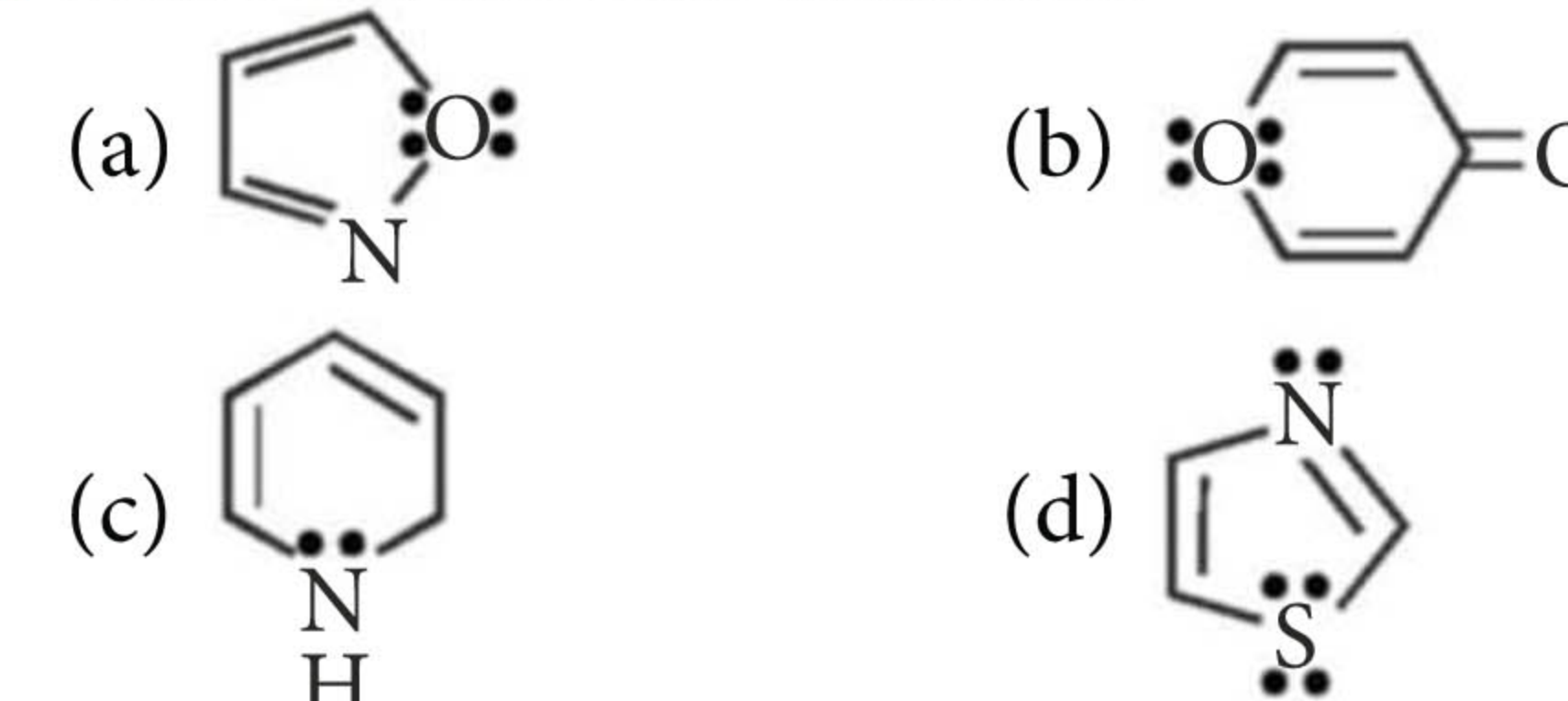
10. Given below in the choices of compounds and reagents which is not needed to synthesize (X)?

- (a) CHBr_3 (b) $t\text{-BuOK}$
(c) CH_2Cl_2 (d)

11. When acetylene is passed through methanol at $160-200^\circ\text{C}$ in the presence of a small amount of potassium methoxide and under pressure, which of the following is formed?

- (a) Polyvinyl alcohol (b) Divinyl ether
(c) Dimethyl ether (d) Methyl vinyl ether

12. Mark out the non-aromatic.



Assertion & Reason Type

Directions : In the following questions, a statement of assertion is followed by a statement of reason. Mark the correct choice as :

- (a) If both assertion and reason are true and reason is the correct explanation of assertion.
(b) If both assertion and reason are true but reason is not the correct explanation of assertion.
(c) If assertion is true but reason is false.
(d) If both assertion and reason are false.

13. **Assertion :** Isomerisation also result when NaNH_2 is used in the dehydrobromination of 2, 2-dibromobutane forming 2-butyne as well as 1-butyne.

Reason : All possible triple-bond isomers are formed, but NaNH_2 is such a strong base that it deprotonates the terminal acetylene, removing it from the equilibrium.

14. **Assertion :** Melting point of *neo*-pentane is higher than that of *n*-pentane but the boiling point of *n*-pentane is higher than that of *neo*-pentane.

Reason : Melting point depends upon packing of molecules in the crystal lattice while boiling point depends upon surface area of the molecules.

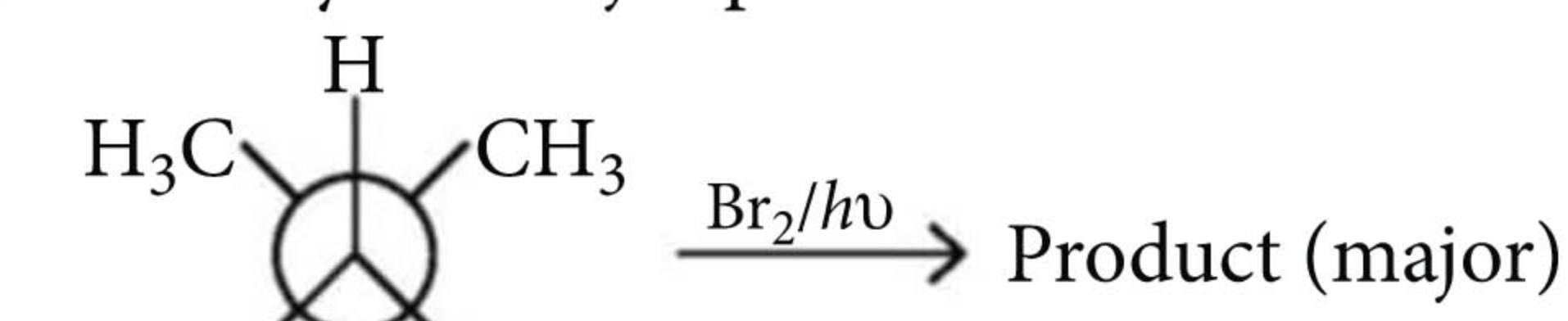
15. **Assertion :** Nitrobenzene reacts faster than benzene in electrophilic bromination.

Reason : Because of unsaturation, benzene easily undergoes addition reactions.

JEE MAIN / ADVANCED

Only One Option Correct Type

16. Identify the major product.



- (a) $\text{CH}_3\text{C}(\text{CH}_3)_2\text{CH}_2\text{Br}$ (b) $\text{CH}_3\text{C}(\text{CH}_3)_2\text{CH}_2\text{Br}$
(c) $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$ (d) $\text{CH}_3\text{CH}(\text{Br})\text{CH}_3$

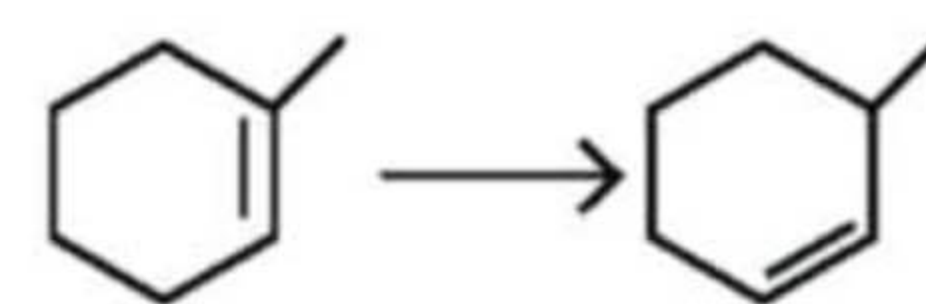
COMIC CAPSULE

What's the difference between chemistry jokes and physics jokes?

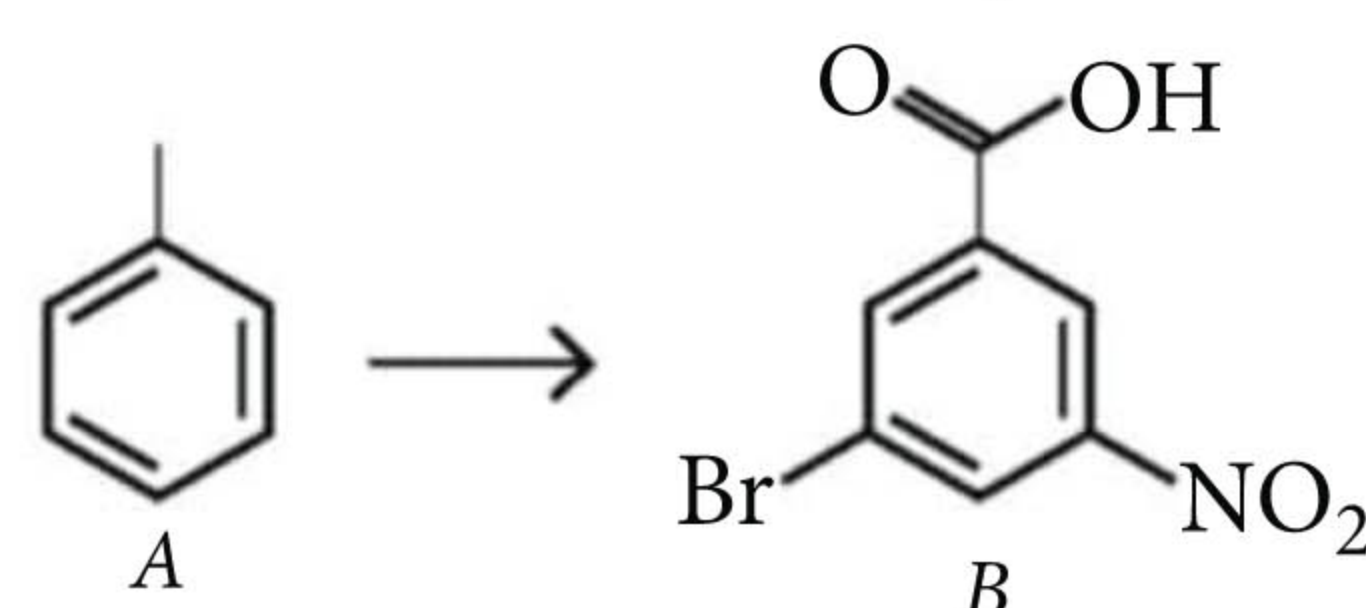
Chemistry jokes can be funny periodically, but physics jokes have more potential.



17. Which reagent is best to perform the following transformation?



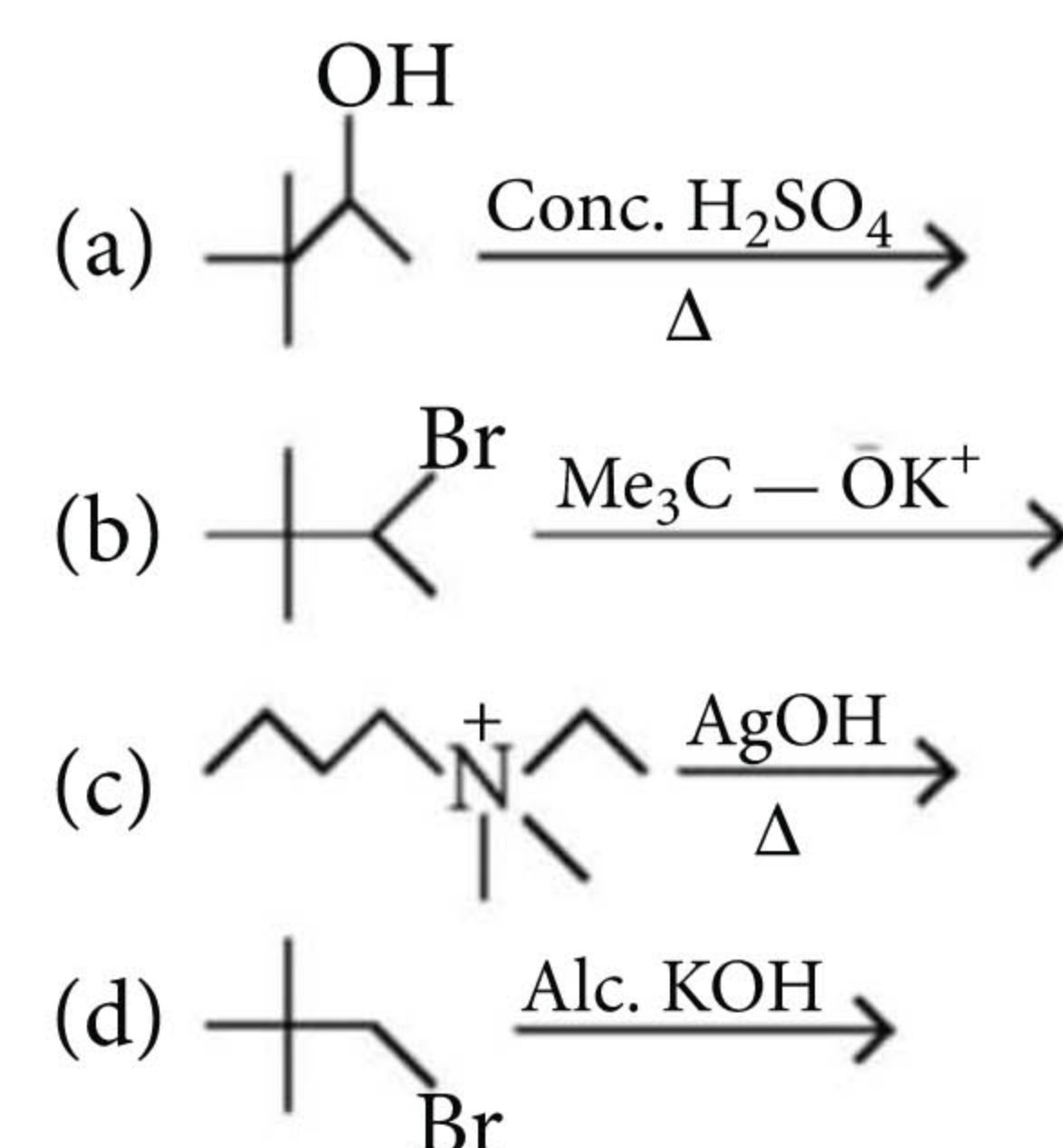
- (a) HBr, NaOH
(b) HBr, $R-O-O-R$, $h\nu$; Me_3COK^+
(c) $BH_3 \cdot THF$, NaOH — H_2O_2
(d) Br_2 , NaOH
18. Given reaction can be performed by using reagents



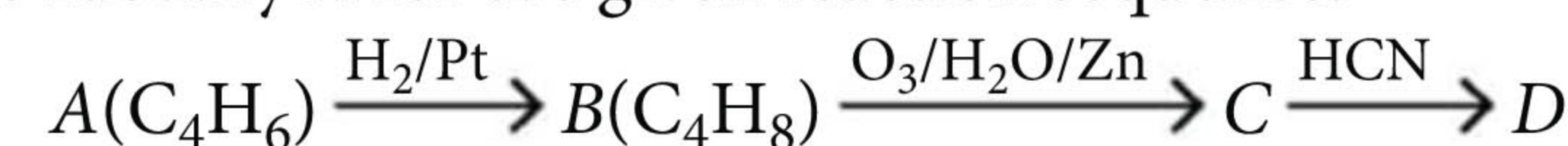
- (I) $Br_2/FeBr_3$
(II) HNO_3/H_2SO_4
(III) $K_2Cr_2O_7/H_2SO_4, \Delta$
These reagents should be used in following order
(a) $A \xrightarrow{III} \xrightarrow{II} \xrightarrow{I} B$ (b) $A \xrightarrow{II} \xrightarrow{I} \xrightarrow{III} B$
(c) $A \xrightarrow{I} \xrightarrow{II} \xrightarrow{III} B$ (d) $A \xrightarrow{II} \xrightarrow{III} \xrightarrow{I} B$
19. Which of the following is the correct decreasing order of decarboxylation on heating with sodalime?
- I. CF_3CH_2COONa II. CF_3COONa
III. $Cl_3CCOONa$ IV. CCl_3CH_2COONa
V. CH_3CH_2COONa VI. CH_3COONa
(a) $II > III > I > IV > VI > V$
(b) $III > I > IV > VI > V > II$
(c) $II > III > VI > I > IV > V$
(d) $III > II > IV > I > V > VI$

More than One Options Correct Type

20. Which of the following reactions will give least substituted alkene?



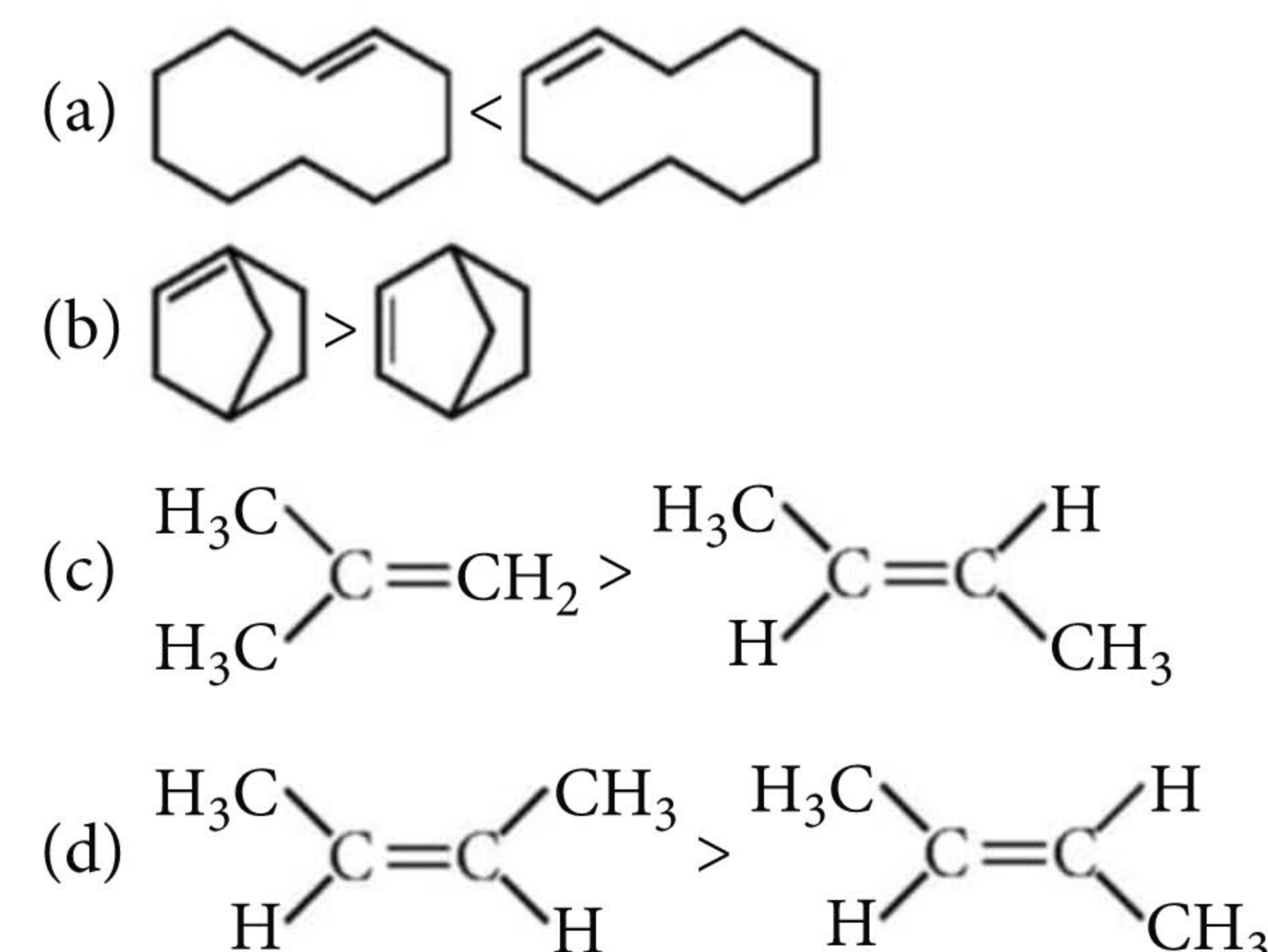
21. Identify A for the given reaction sequence.



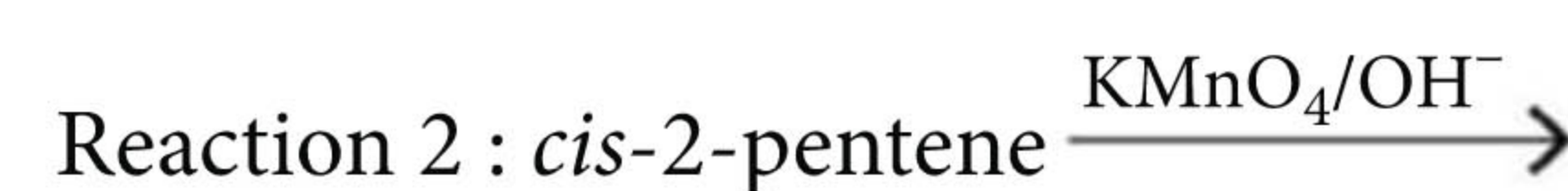
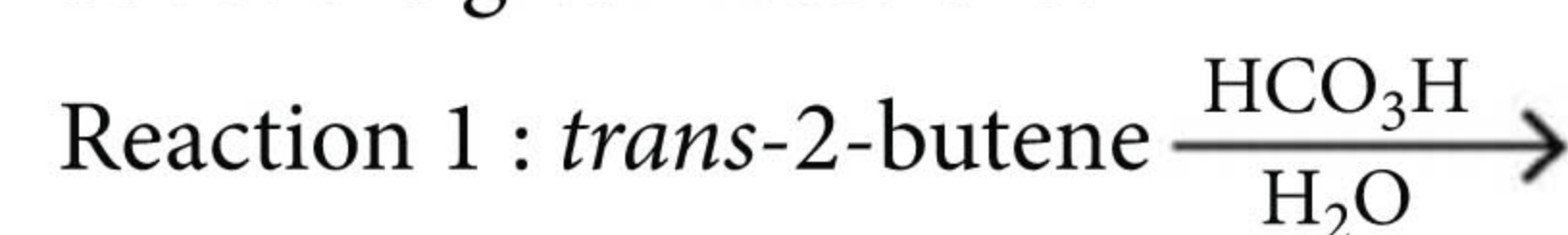
D has chiral carbon and can be hydrolysed to lactic acid.

- (a) $CH_3-C \equiv C-CH_3$
(b) $CH_2=CH-CH=CH_2$
(c) (d)

22. Which of the following orders are correct regarding stability?



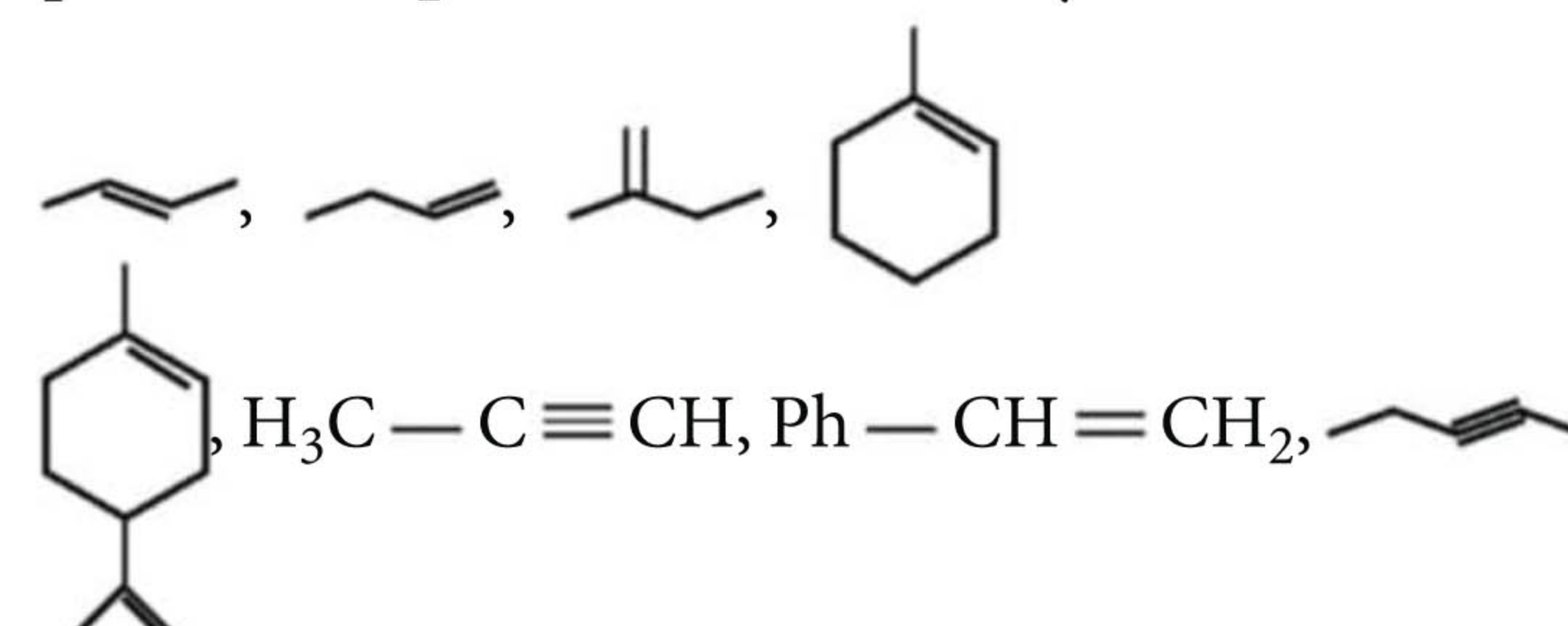
23. Which of the following statements are incorrect about the given reactions?



- (a) Reaction 1 leads to racemic mixture.
(b) Reaction 1 produces optically inactive compound.
(c) Reaction 2 yields meso compound.
(d) Reaction 1 and 2 give same product.

Numerical Value Type

24. Examine the structural formulas of the following compounds and find how many compounds will produce CO_2 on oxidative ozonolysis.



25. How many reagents from the list below give effervescence when reacted with 1-pentyne?
- $NaOH$, CH_3CH_2ONa , CH_3CH_2MgBr ,
 NaH , $NaNH_2$, Na , $NaHCO_3$, $((CH_3)_2CH)_2NLi$,
 CH_3CH_2Li , C_6H_5Li

26. Number of alkynes that on catalytic reduction gives 3-ethyl-4-methylheptane is

Matrix Match Type

Answer the following questions (27 and 28) by appropriately matching the columns based on the information given in the passage :

Alkenes react with diborane (B_2H_6) in the presence of ether to form trialkyl boranes, which upon subsequent treatment with $H_2O_2/\bar{O}H$ gives alcohols corresponding to anti-Markovnikov's addition of H_2O to alkenes, with *syn*-addition. No rearrangement takes place. It proceeds *via* cyclic transition state. Any one of the following ethers as solvent may be used.

THF (tetrahydrofuran,)

Diethyl ether ($Me-O-Me$)

Dimethyl ether ($Me-O-Me$)

Diglyme ($Me-O-CH_2CH_2-O-Me$)

	Column-I		Column-II
P.	$\xrightarrow[2. CH_3COOH]{1. B_2H_6}$	I	
Q.	$\xrightarrow[2. H_2O_2, OH^-]{1. B_2H_6}$	II	
R.	$\xrightarrow[2. K_2Cr_2O_7]{1. B_2H_6/H_2O_2/OH^-}$	III	
S.	$\xrightarrow[2. CO, H_2O/OH^-]{1. B_2H_6}$	IV	

27. Which of the following has the correct combination considering column I and column II?

- (a) P, I (b) Q, IV
(c) R, III (d) S, II

28. Which of the following has the correct combination considering column I and column II?

- (a) P, II (b) Q, IV (c) R, I (d) S, III

Answer the following questions (29 and 30) by appropriately matching the columns based on the information given in the passage :

Huckel Rule : This is also known as the $(4n + 2)$ rule and was proposed by Erich Huckel in 1931. A compound will be aromatic if it obeys the following points :
The molecule or ion should be cyclic and planar.

There should be a cyclic cloud of delocalised π -electrons, surrounding all carbon atoms of the cyclic system above and below the plane.

The π -electron cloud must contain a total of $(4n + 2)$ π -electrons, where n is an integer with values 0, 1, 2, 3,etc.

	Column-I (Molecule)		Column-II (Characteristics)
P.		I	Planar
Q.		II	p -orbitals form extended π -bonding
R.		III	$(4n + 2) \pi e^-$ rule
S.		IV	$(4n) \pi e^-$ rule

29. Which of the following has the correct combination considering column I and column II?

- (a) P, I, II, IV (b) Q, I, II, IV
(c) R, I, IV (d) S, III, IV

30. Which of the following has the correct combination considering column I and column II?

- (a) P, I, IV (b) Q, III, II
(c) R, II, IV (d) S, I, IV

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CHECK YOUR PERFORMANCE

	No. of questions attempted	No. of questions correct	Marks scored in percentage	If your score is	
	$> 80\%$	Your preparation is going good, keep it up to get high score.
				60-80%	Need more practice, try hard to score more next time.
				$< 60\%$	Stress more on concepts and revise thoroughly.

GET SET GO NEET



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- The vapour pressure of the solution of two liquids $A(p^\circ = 80 \text{ mm})$ and $B(p^\circ = 120 \text{ mm})$ is found to be 100 mm of Hg when $x_A = 0.4$. The result shows that
(a) solution exhibits ideal behaviour
(b) $\Delta H_{\text{solution}} < 0$
(c) solution shows positive deviation
(d) solution will show positive deviation for lower concentration and negative deviation for higher concentration.
- The pyrolysis of an organic ester follows a first order process and its rate constant can be expressed as $\ln k = 78.09 - \frac{42075}{T}$ where, unit of k is min^{-1} . Calculate the time required for 25 per cent reaction to complete at 227°C .
(a) 102.5 min (b) 85 min
(c) 123 min (d) 100 min
- Consider the cell,
 $\text{Ag}_{(s)}|\text{AgBr}_{(s)}|\text{Br}^-_{(aq)}||\text{AgCl}_{(s)}|\text{Cl}^-_{(aq)}|\text{Ag}_{(s)}$ at 25°C . The solubility product constants of AgBr and AgCl are respectively 5×10^{-13} and 1×10^{-10} . Then what would be the ratio of the concentrations of Br^- and Cl^- ions when emf of the cell will be zero?
(a) 1 : 200 (b) 1 : 100 (c) 1 : 500 (d) 200 : 1
- $\text{C}_4\text{H}_{11}\text{N}$ on reaction with HNO_2 forms a tertiary alcohol. Thus, $\text{C}_4\text{H}_{11}\text{N}$ is
(a) primary amine (b) secondary amine
(c) tertiary amine (d) quaternary ammonium salt.
- Which will be the correct product for the following reaction?

(a) (b)
(c) (d)
- Consider the following reactions :
Reaction I:
Reaction II:

Which of the following is a correct comparison of rate of reaction?

- $r_I > r_{II}$
 - $r_I < r_{II}$
 - $r_I = r_{II}$
 - Reactions are not possible.
- Which of the following statements are correct?
(1) Atoms on a body diagonal are inside the cube and are shared by adjacent atoms.
(2) Atoms on a face diagonal are shared by two unit cells and only 1/2 of each atom belongs to each unit cell.
(3) Atoms on a body diagonal are inside the cube and are not shared by any adjacent atoms.
(4) Total number of atoms in a unit cell
 $= \frac{n_c}{8} + \frac{n_f}{4} + \frac{n_b}{2} + \frac{n_e}{4}$ where, n_c , n_f , n_b and n_e are number of atoms at the corner, face centre, body centre and edge centre of a unit cell respectively.
(a) 1 and 2 (b) 1 and 4
(c) 2 and 3 (d) 2 and 4
 - Select the correct statement among the following.
(1) For the phenomenon of adsorption, $\Delta G < 0$.
(2) At high concentration of soap in water, soap behaves as associated colloid.
(3) The term 'sorption' stands for adsorption.
(4) At the equilibrium position in the process of adsorption, $\Delta H = T\Delta S$.
(a) 1 and 3 (b) 1, 2 and 4
(c) 2 and 3 (d) All of these
 - What is product of the following reaction?

(a) (b)
(c) (d) None of these
 - Which of the following statements is not correct?
(a) Allergic conditions are cured by antihistamines.
(b) Hormones are continuously produced but not stored in the body.
(c) Catabolism involves degradation of molecules.
(d) The function of the white blood cells is to protect the body against infections.
 - Red coloured oxide (M) whose cation has pseudo inert electronic configuration reacts with air to give another oxide (N) which is black in colour. When sulphate of its metal is reacted with $\text{K}_4[\text{Fe}(\text{CN})_6]$ it produces brown precipitate. Select the correct statement.
(a) The brown precipitate formed is $\text{Cu}_2[\text{Fe}(\text{CN})_6]$.
(b) The red coloured oxide (M) is Cu_2O .
(c) The black coloured oxide (N) is CuO .
(d) All of the above.
 - Which nitrogen take part in the semicarbazone formation with the carbonyl group when the nucleophile is $\text{NH}_2 - \text{NH} - \text{C}(=\text{O}) - \text{NH}_2$?
(a) y -Nitrogen (b) x -Nitrogen
(c) z -Nitrogen (d) All of these.
 - Which of the following is incorrect statement regarding
 $A = [\text{Co}(\text{en})_2\text{Cl}_2]^+$ and $B = [\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$?
(a) A is more thermodynamically stable than B .
(b) A shows optical isomerism.
(c) A and B both are diamagnetic.
(d) A is an outer orbital complex while B is an inner orbital complex.
 - D -glyceraldehyde $\xrightarrow[\text{HCl}]{\text{Me}_2\text{CO}}$ A
 $\xrightarrow[\text{CH}_2=\text{CHMgCl}]{\text{O}_3}$ $B \xrightarrow{\text{O}_3}$ C
The final product ' C ' is
(a) L -glyceraldehyde (b) D -erythrose
(c) D -arabinose (d) D -glucose.
 - Which of the following statements are correct?
1. NO acts both as an oxidising as well as reducing agent.
2. N_2O_5 with alkalis gives nitrates.
3. Moist NH_3 gas is dried over CaCl_2 .
4. Action of NH_3 on excess of Cl_2 gives NH_4Cl as stable product.
(a) Only 1 and 2 (b) Only 2 and 3
(c) Only 1 and 3 (d) Only 3 and 4

SOLUTIONS

- (b) : $P = 0.4 \times 80 + 0.6 \times 120 = 104$
 $P_{\text{Total}} = 100 \text{ mm of Hg}$
 $\therefore P_{\text{Total}} < x_A P_A^\circ + x_B P_B^\circ \Rightarrow \Delta H_{\text{solution}} < 0$
- (c) : $\ln k = 78.09 - \frac{42075}{500} = -6.06$
 $\log k = -\frac{6.06}{2.303} = -2.63; k = 2.344 \times 10^{-3} \text{ min}^{-1}$
when $x = 0.25; k = \frac{2.303}{t_{1/4}} \log \frac{a}{0.75a}$
 $t_{1/4} = \frac{2.303}{2.344 \times 10^{-3}} \log 1.333 = 122.64 \text{ min}$

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Unit
3

General Principles and Processes of Isolation of Elements | The p-Block Elements (Group 15 to 18)

General Principles and Processes of Isolation of Elements

METALLURGY

- The natural substances in which the metals occur in the earth along with impurities are called minerals.
- The minerals from which the metals can be conveniently and economically extracted are called ores. Thus all ores are minerals but all minerals are not ores.
- An ore is contaminated with earthly or undesired materials known as gangue.
- The entire scientific and technological process used for isolation of the metal from its ores is known as metallurgy.

Types of Ores and their Examples

S. No.	Types of Ore	Examples
1.	Native metals	Cu, Ag, Au, As, Sb, Bi, Pd, Pt
2.	Oxides	Al ₂ O ₃ , Fe ₂ O ₃ , Fe ₃ O ₄ , SnO ₂ , MnO ₂ , TiO ₂ , FeO, Cr ₂ O ₃
3.	Carbonates	CaCO ₃ , MgCO ₃ , FeCO ₃ , PbCO ₃ , BaCO ₃ , SrCO ₃ , ZnCO ₃
4.	Halides	NaCl, KCl, AgCl, MgCl ₂ ·6H ₂ O
5.	Sulphides	Ag ₂ S, Cu ₂ S, CuS, PbS, ZnS, HgS

6.	Sulphates	BaSO ₄ , PbSO ₄ , CaSO ₄ ·2H ₂ O, CuSO ₄ ·2Cu(OH) ₂
7.	Silicates	Be ₂ AlSi ₆ O ₁₈
8.	Phosphates	CePO ₄ , LaPO ₄ , NdPO ₄ , PrPO ₄

STEPS INVOLVED IN METALLURGY

- Crushing the ore
- Dressing or concentration of the ore
- Isolation of the metal from the concentrated ore
- Purification or refining

Crushing the Ore

- The lumps of ores are broken into small pieces with the help of crushers or grinders.

Concentration of Ore

- The removal of undesired impurities (gangue) from the ores is known as concentration or dressing or benefaction. It can be done by both physical and chemical processes.

Physical Methods

- Gravity separation :** This method is used for concentration of oxide and carbonate ores and separation is based on the difference in the specific

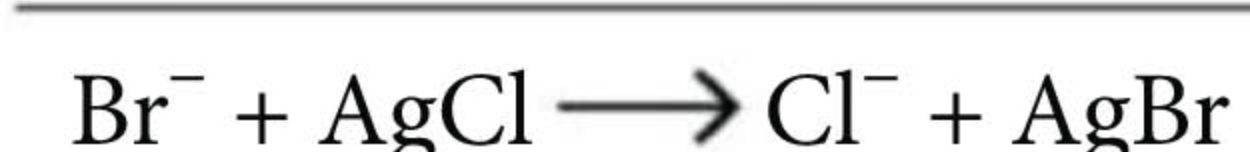
3. (a) : $E_{\text{Br}^-/\text{AgBr}/\text{Ag}}^\circ = E_{\text{Ag}^+/\text{Ag}}^\circ + \frac{0.059}{1} \log K_{sp}(\text{AgBr})$

$$= E_{\text{Ag}^+/\text{Ag}}^\circ - 0.7257$$

and $E_{\text{Cl}^-/\text{AgCl}/\text{Ag}}^\circ = E_{\text{Ag}^+/\text{Ag}}^\circ + \frac{0.059}{1} \log K_{sp}(\text{AgCl})$

$$= E_{\text{Ag}^+/\text{Ag}}^\circ - 0.59$$

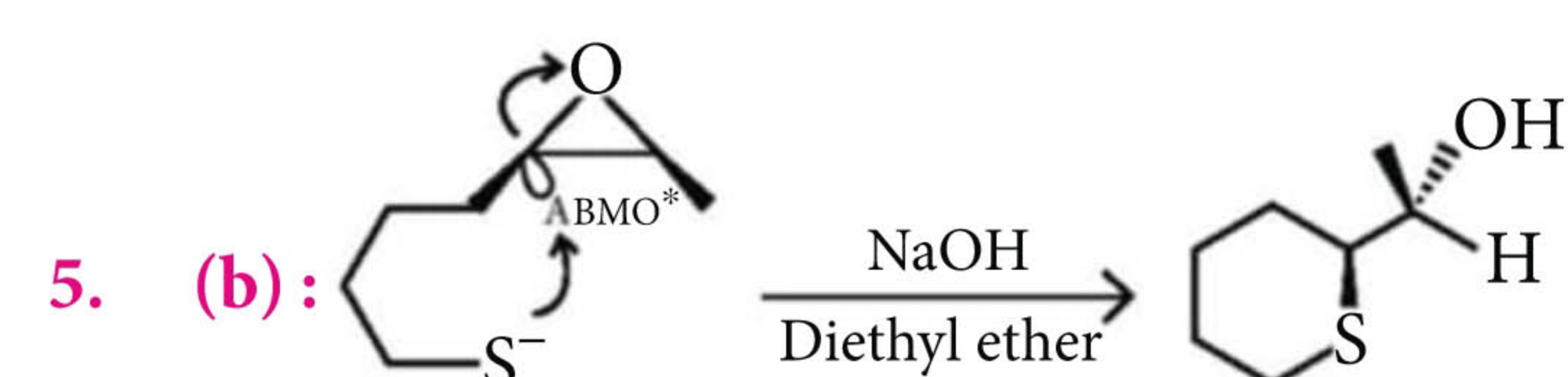
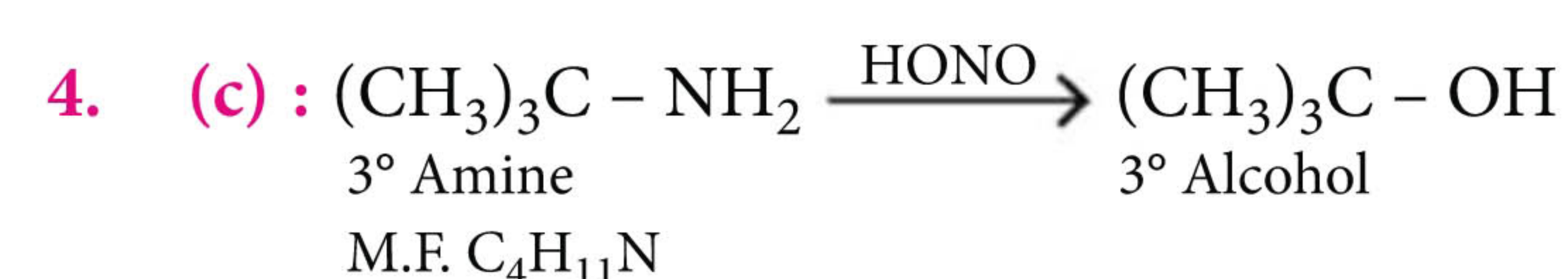
Now cell reaction is



$$E_{\text{cell}}^\circ = E_{\text{Cl}^-/\text{AgCl}/\text{Ag}}^\circ - E_{\text{Br}^-/\text{AgBr}/\text{Ag}}^\circ$$

$$0 = (0.7257 - 0.59) + \frac{0.059}{1} \log \frac{[\text{Br}^-]}{[\text{Cl}^-]}$$

$$\Rightarrow \frac{[\text{Br}^-]}{[\text{Cl}^-]} = 0.005 \Rightarrow 1 : 200$$

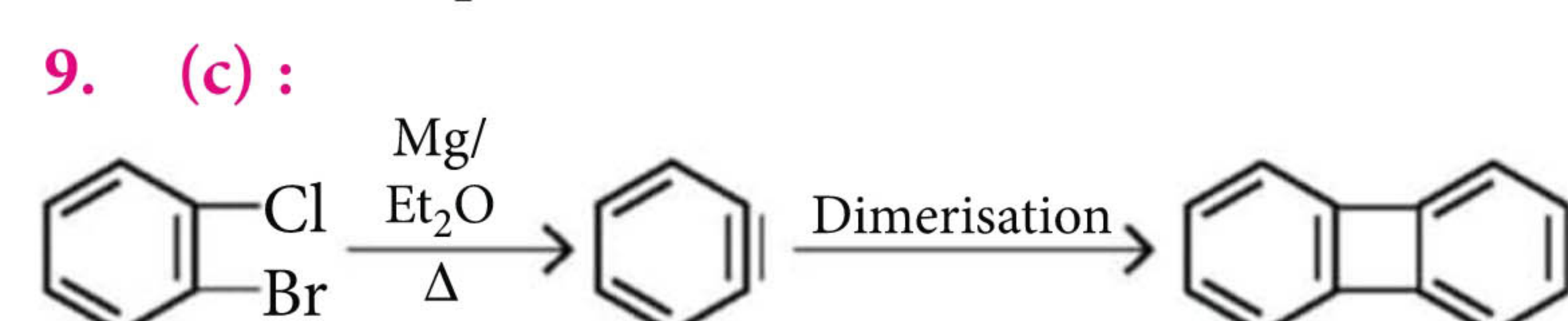


6. (a) : The reactive species is the nitrosonium ion (electrophile) and the most likely site of attack will be that with the highest electron density. Such kind of delocalisation is not found in 2,6-dimethyl derivative due to steric inhibition of resonance.

7. (c) : Total number of atoms in a unit cell

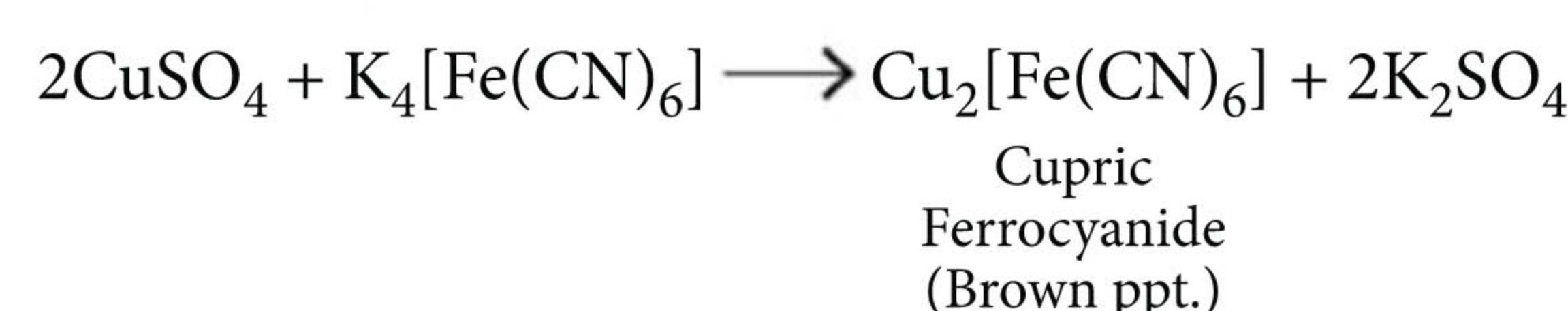
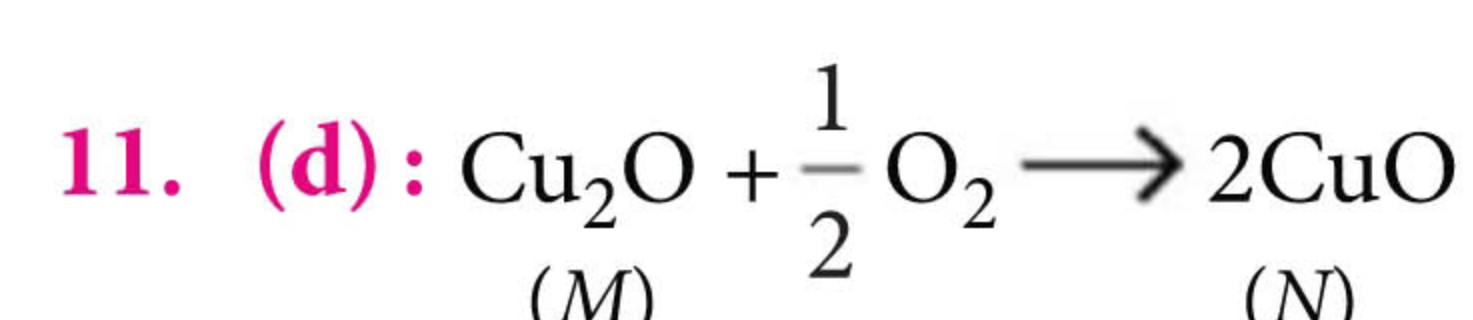
$$= \frac{n_c}{8} + \frac{n_f}{2} + \frac{n_b}{1} + \frac{n_e}{4}$$

8. (b) : The term 'sorption' stands for both adsorption and absorption.

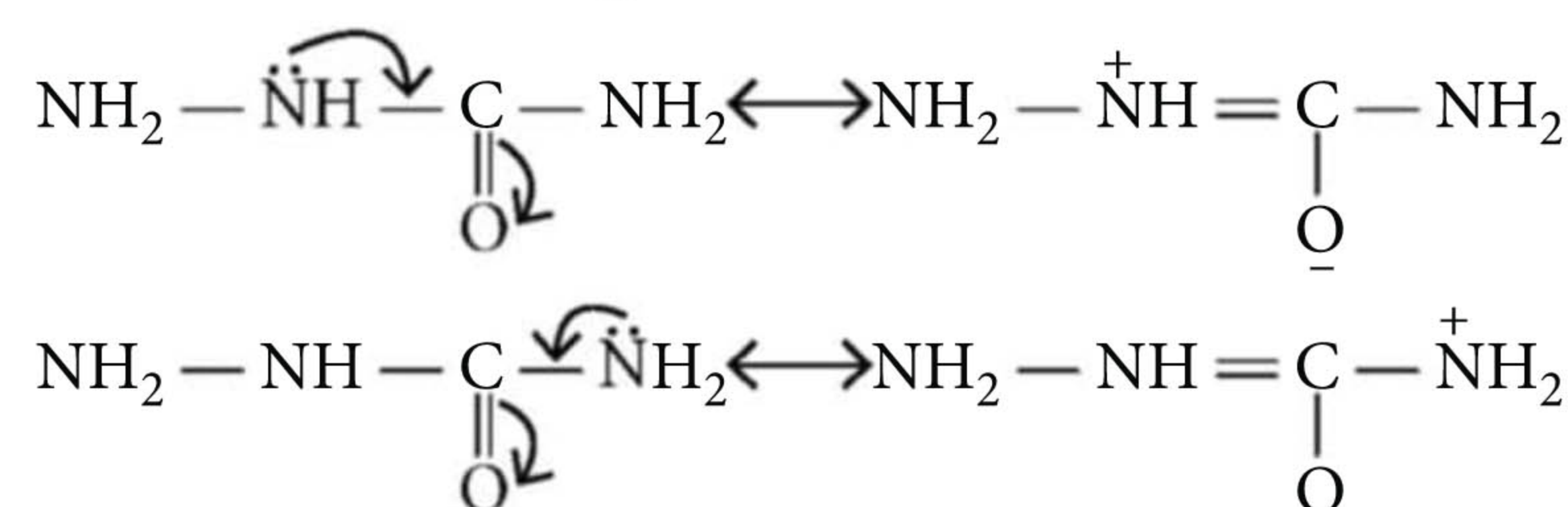
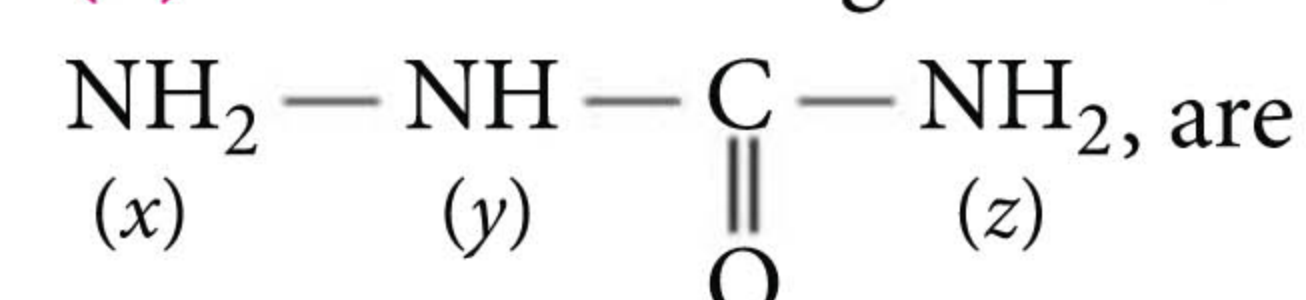


Ortho-dihalobenzene does not form Grignard reagent.

10. (b) : Hormones are not continuously produced, rather they are produced in a controlled manner according to the requirement of the body.

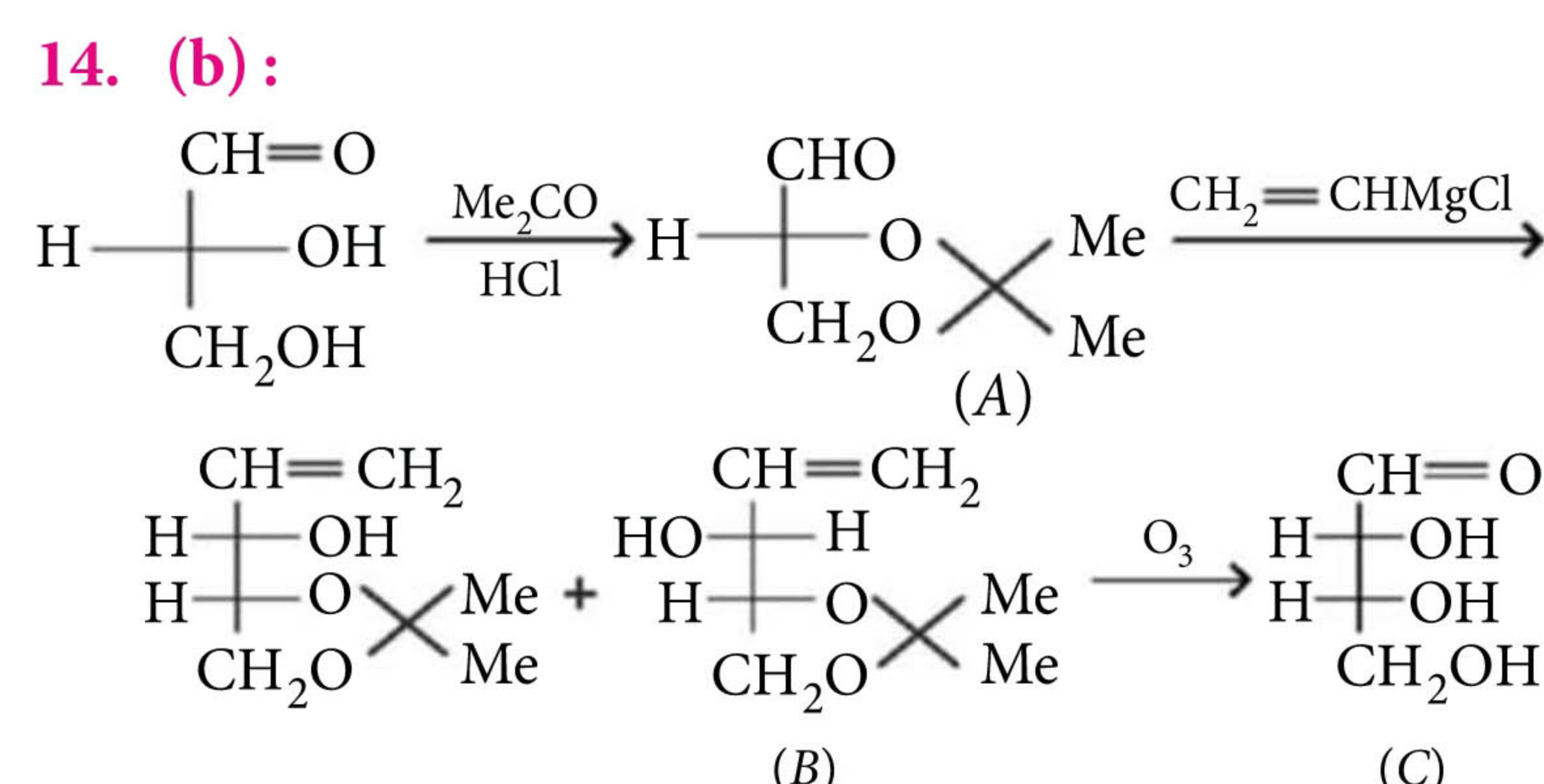


12. (b) : The resonating structures of nucleophile,



Hence, the lone pair of electrons on nitrogen (y) and (z) are not available due to involvement in resonance, so only the lone pair of electrons on nitrogen (x) is free to take part in semi-carbazone formation.

13. (d) : Due to chelate effect, A is more thermodynamically stable.
Cis-isomer of $[\text{Co}(\text{en})_2\text{Cl}_2]^+$ shows optical isomerism.
 $\text{Co}^{3+} = 3d^6$, all electrons are paired hence, diamagnetic.
 (A) and (B) both are inner orbital complexes.



15. (a) : (a) Nitric oxide acts both as an oxidising as well as a reducing agent while all other nitrogen oxide acts as oxidising agents only.
 (b) $\text{N}_2\text{O}_5 + 2\text{NaOH} \longrightarrow 2\text{NaNO}_3 + \text{H}_2\text{O}$
 (c) The moisture present in ammonia may be removed by passing through a glass tower packed with quick lime, CaO.
 (d) With excess of Cl₂, nitrogen trichloride and hydrogen chloride are formed.
 $\text{NH}_3 + 3\text{Cl}_2 \longrightarrow \text{NCl}_3 + 3\text{HCl}$

gravities of the gangue and ore particles. Generally oxide and carbonates ores are concentrated by this method *e.g.*, cassiterite and haematite.

- **Magnetic separation** : It is useful when one component, either the ore or the impurity is magnetic in nature. Ferro-magnetic ores are concentrated by this method. *e.g.*, wolframite (FeWO_4) is separated from cassiterite (SnO_2) by this method.
- **Froth floatation** : Dense sulphide ores are concentrated by this method, and it is based on the preferential wetting properties of the ore and gangue particles with frothing agent and water. It is used to concentrate the dense ores such as galena and zinc blende.

Chemical Methods

- Chemical methods like leaching is used if the ore is soluble in some suitable solvent. This method involves the treatment of the ore with suitable reagent so as to make it soluble while impurities remain insoluble, and the ore is recovered from the solution by suitable chemical method.
 - Leaching of alumina from bauxite ore :

$$\text{Al}_2\text{O}_3 + 2\text{NaOH} \longrightarrow 2\text{NaAlO}_2 + \text{H}_2\text{O}$$

$$\text{NaAlO}_2 + 2\text{H}_2\text{O} \longrightarrow \text{Al}(\text{OH})_3 + \text{NaOH}$$

$$2\text{Al}(\text{OH})_3 \xrightarrow{\Delta} \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O}$$
 - Mac Arthur Forest cyanide process is used for extraction of Au or Ag and is based on the principle of leaching. *e.g.*,

$$4\text{Ag} + 8\text{NaCN} + 2\text{H}_2\text{O} + \text{O}_2 \longrightarrow 4\text{Na}[\text{Ag}(\text{CN})_2] + 4\text{NaOH}$$

Sod. argentocyanide

$$2\text{NaAg}(\text{CN})_2 + \text{Zn} \longrightarrow \text{Na}_2[\text{Zn}(\text{CN})_4] + 2\text{Ag}\downarrow$$

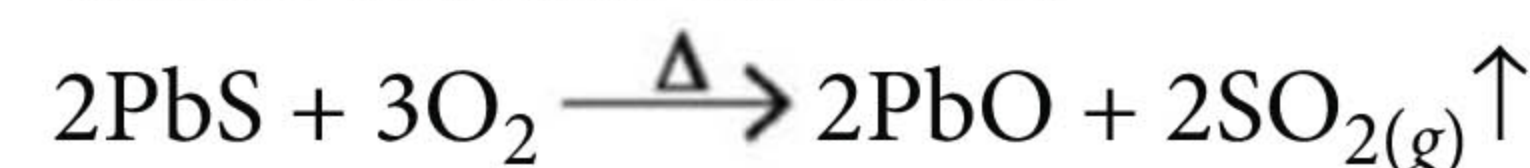
Soluble

Isolation of the Metal from the Concentrated Ore

- Metals are usually extracted by reduction. Thus, the concentrated ores is converted into a ore which is suitable for reduction. Thus, isolation involves two major steps :
 - Conversion of ore into metal oxide**
 - The methods used are
 - **Calcination** : The process of converting concentrated ore into oxide by heating it strongly below its melting point in the absence of air is called calcination.

$$\text{ZnCO}_3 \xrightarrow{\Delta} \text{ZnO} + \text{CO}_2\uparrow$$
 - **Roasting** : In this process the concentrated ore (usually sulphide) is heated strongly, in the

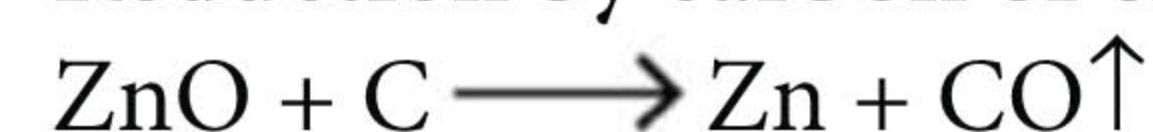
presence of excess of air so that sulphide ore is converted into its oxide.



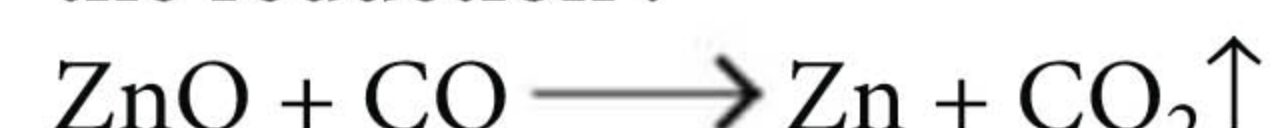
II. Reduction of metal oxides

• Chemical reduction

– Reduction by carbon or smelting :



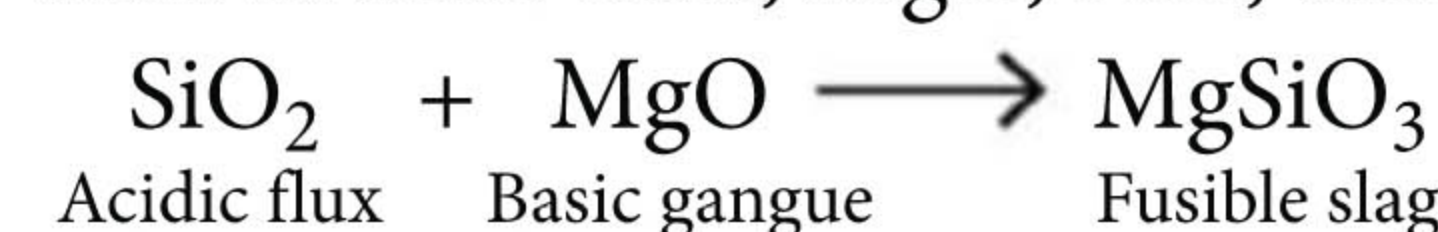
Released carbon monoxide also brings about the reduction :



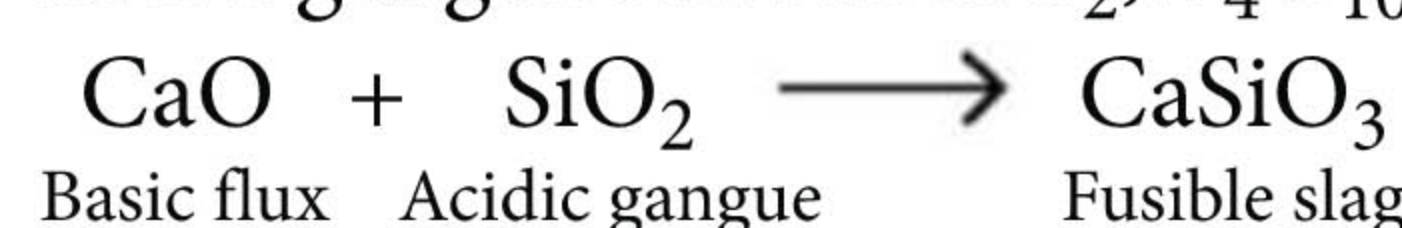
Smelting is carried out in blast furnace at high temperature. So, that metal is produced in liquid state. Sometimes metal is obtained in vapour state, *e.g.*, Zn.

- **Flux** : To remove the infusible impurity (gangue) from calcined or roasted ore, certain substances are mixed with concentrated ore which combine with earthy impurities to form easily fusible mass called slag. There are two types of flux :

(i) **Acidic flux** : Acidic fluxes like silica (SiO_2) and borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) are used to remove basic earthy impurities (gangue) such as lime CaO , MgO , FeO , etc.



(ii) **Basic flux** : Basic fluxes like lime (CaO), magnesium oxide (MgO) are used to remove acidic gangue such as SiO_2 , P_4O_{10} , etc.



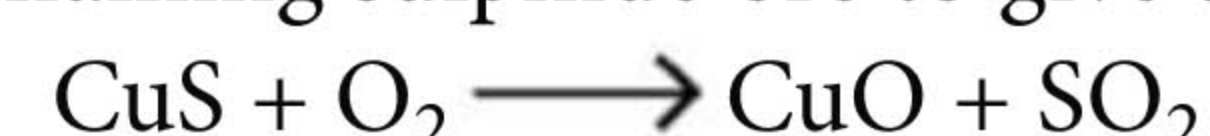
- **Aluminium reduction method (Aluminothermy or Goldschmidt thermite process)** : This is the process of reducing certain metal oxides which cannot be reduced by carbon like TiO_2 , Cr_2O_3 and Mn_3O_4 etc., by using aluminium powder as reducing agent.

$$\text{Cr}_2\text{O}_3 + 2\text{Al} \longrightarrow 2\text{Cr} + \text{Al}_2\text{O}_3 + \text{Heat}$$

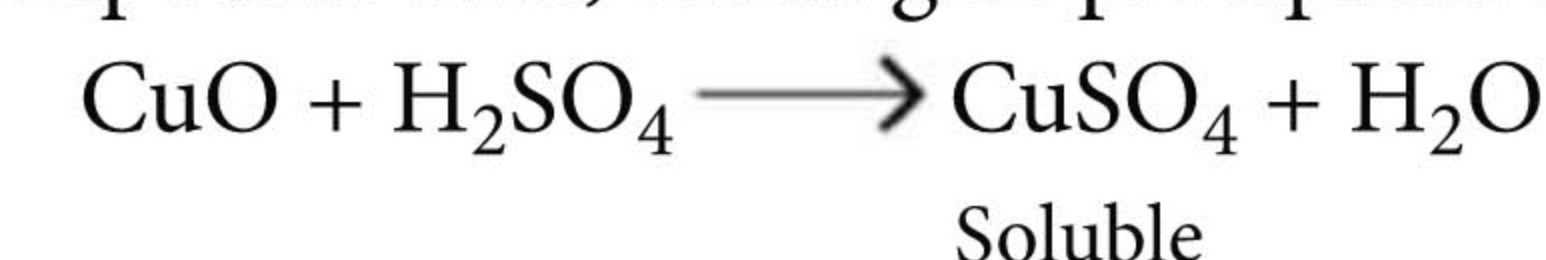
$$3\text{Mn}_3\text{O}_4 + 8\text{Al} \longrightarrow 4\text{Al}_2\text{O}_3 + 9\text{Mn} + \text{Heat}$$

Metal halides can also be reduced to metal (Kroll's process).

- **Self-reduction method** : When the sulphide ores of less electropositive metals like Hg, Cu, Pb, Sb, etc., are heated in air, a part of the ore gets oxidized to oxide or sulphate, which then reacts with the remaining sulphide ore to give the metal and SO_2 .



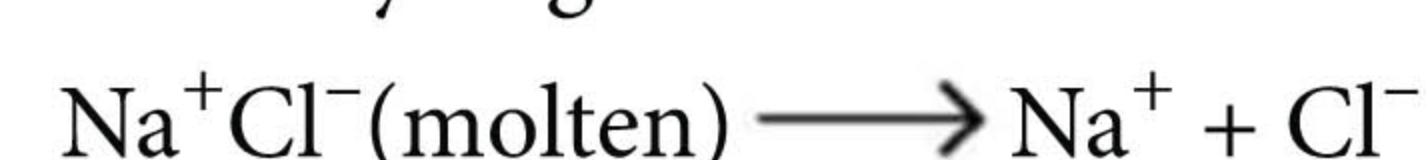
- **Hydrometallurgy or Precipitation** : In this process, ore is treated with such chemical reagent that converts it to some soluble compound. Now addition of a more electropositive metal to the filtrate displaces less electropositive metal from the compound thus, metal gets precipitated.



Ag and Au are also recovered from the solution of their complex cyanide salts by zinc scrap.

- **Electrolytic reduction** : Highly reactive metals are reduced from their corresponding cations by electrolytic reduction. Al, Na, Mg, K, Ca, etc. are obtained by electrolysis of their molten oxides, halides, etc. These metals cannot be reduced with carbon because at high temperature they form carbides with carbon.

For example, sodium metal is obtained by electrolyzing molten sodium chloride.



Aluminium is also obtained by electrolytic reduction of Al_2O_3 dissolved in cryolite (Na_3AlF_6).

PEEP INTO PREVIOUS YEARS

- The cyanide process of gold extraction involves leaching out gold from its ore with CN^- in the presence of Q in water to form R. Subsequently, R is treated with T to obtain Au and Z. Choose the correct option(s).

(a) R is $[\text{Au}(\text{CN})_4]^-$. (b) T is Zn.
(c) Q is O_2 . (d) Z is $[\text{Zn}(\text{CN})_4]^{2-}$.
(JEE Advanced 2019)
- The composition of 'copper matte' is

(a) $\text{Cu}_2\text{S} + \text{FeS}$ (b) $\text{Cu}_2\text{S} + \text{Cu}_2\text{O}$
(c) $\text{Cu}_2\text{S} + \text{FeO}$ (d) $\text{Cu}_2\text{O} + \text{FeS}$
(Karnataka CET 2016)
- In the extraction of copper from its sulphide ore, the metal is finally obtained by the reduction of cuprous oxide with

(a) carbon monoxide (b) copper (I) sulphide
(c) sulphur dioxide (d) iron (II) sulphide.
(AIPMT 2015, 2012)

ELECTROCHEMICAL PRINCIPLES OF METALLURGY

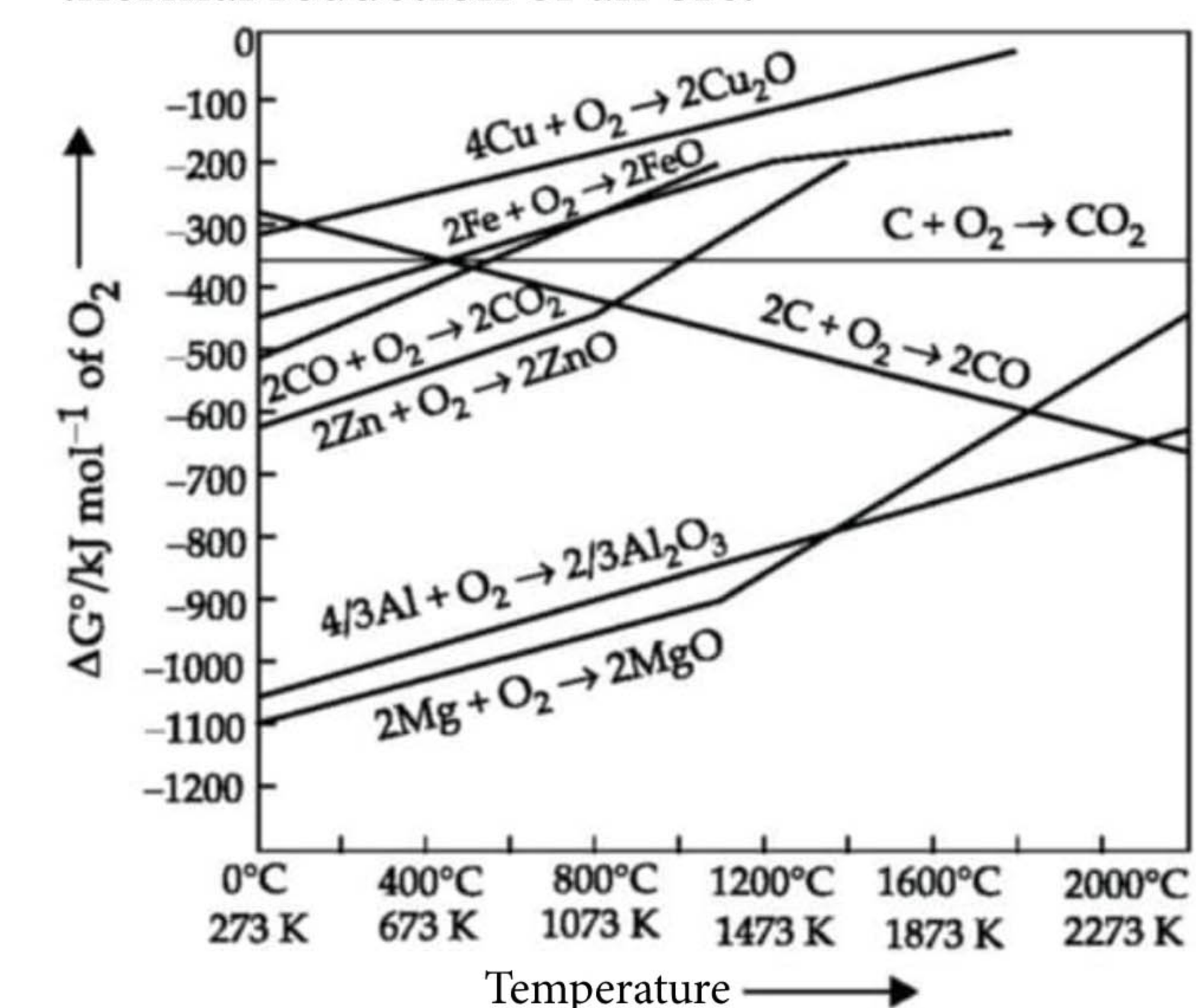
- In the reduction of a molten metal salt, electrolysis is done. Such methods are based on electrochemical principles which can be understood through the equation: $\Delta G^\circ = -nFE^\circ$ where, n = no. of electrons and E° = electrode potential of the redox couple formed in the system. More reactive the metals, higher will be their negative E° values and thus, more difficult is their reduction. If the difference of the two E° values corresponds to a positive value and consequently negative ΔG° value, then the less reactive metal will go into the solution. In simple electrolysis, the M^{n+} ions are discharged at cathode.

$$\text{MO} + \text{C} \longrightarrow \text{M} + \text{CO} ; \Delta G_1 = +ve$$

$$\text{CO} + 1/2\text{O}_2 \longrightarrow \text{CO}_2 ; \Delta G_2 = -ve$$

THERMODYNAMIC PRINCIPLES OF METALLURGY

- The graphical representation of Gibbs energy vs temperature provides a basis for considering the choice of reducing agent in the reduction of oxides. This is known as Ellingham diagram. Such a diagram helps us in predicting the feasibility of thermal reduction of an ore.



Gibbs energy (ΔG°) vs. T plot for formation of some oxides (Ellingham diagram)

- The criterion of feasibility is that at a given temperature, Gibbs energy of reaction must be negative.

Quotable Quote

Anyone who has never made a mistake has never tried anything new.

ALBERT EINSTEIN

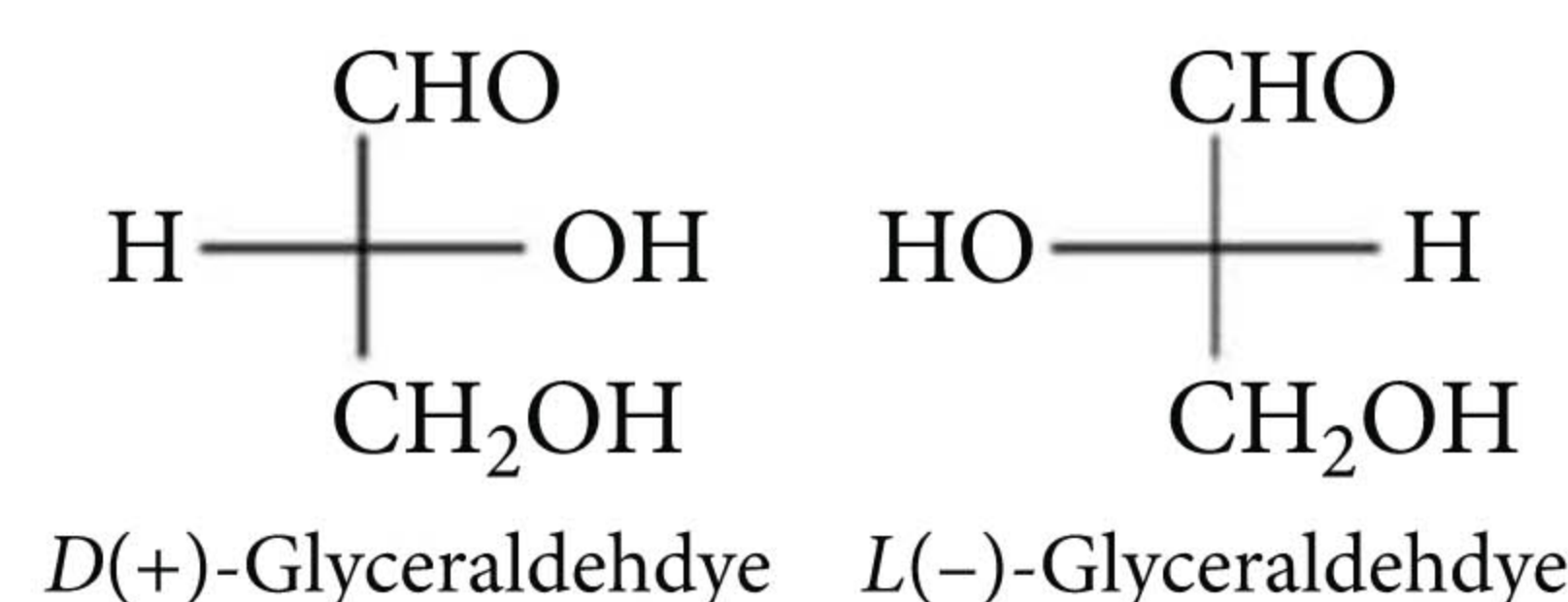
CONCEPT MAP

SPECIFICATION OF CONFIGURATION

The configuration with —OH group at right side is given *D*-configuration arbitrarily whereas the configuration with —OH group at left side is given *L*-configuration.

Chiral molecules which can be chemically related to *D*-glyceraldehyde were designated as *D*-isomer and the molecules related to *L*-glyceraldehyde are designated as *L*-isomer.

In polyhydroxy compounds (sugars) having more than one chiral center, the configuration of stereocenter farthest from carbonyl group is compared with glyceraldehyde configuration.



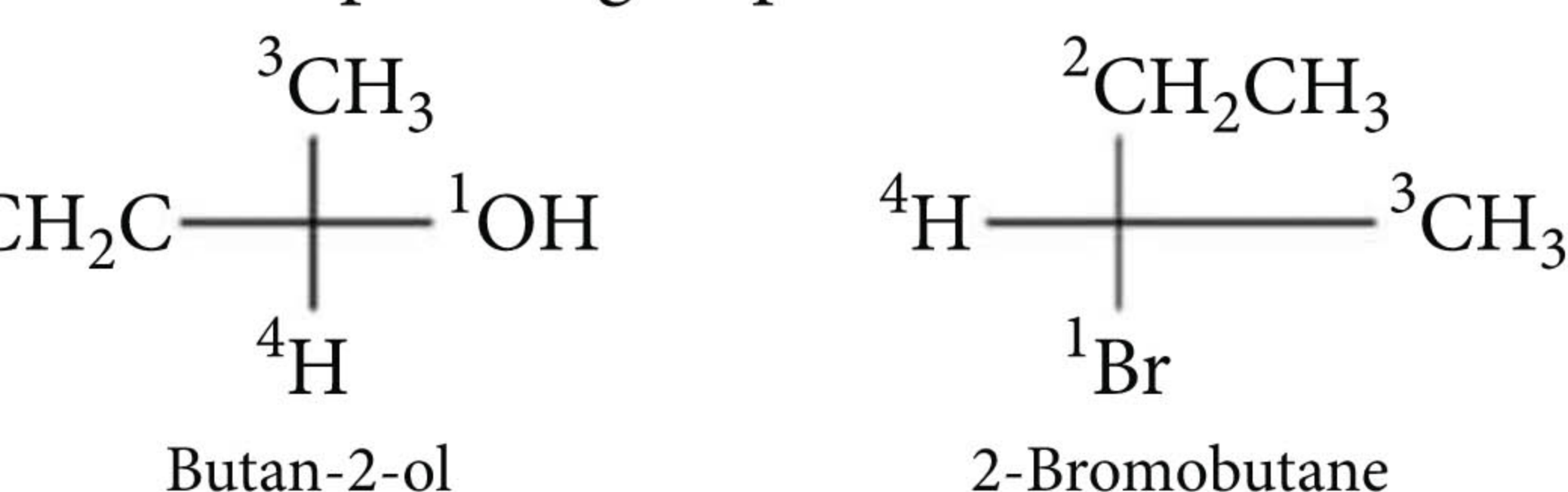
Rules for Assigning Configuration

STEP I : Order of Priority

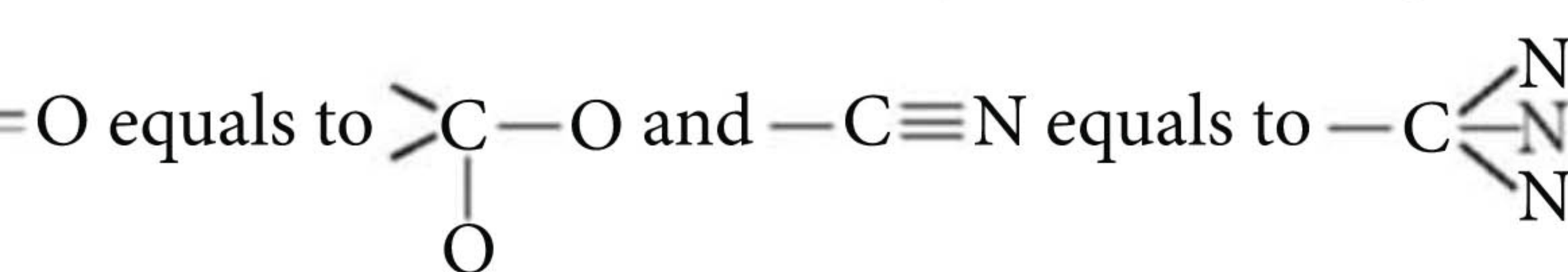
1 : If all the four atoms attached to chirality centre are different, their priority numbers are decided on the basis of their higher atomic numbers.

—I > —Br > —Cl > —F > —O > —N > —C > —H

2 : If two of the atoms attached to chirality centre are same then the relative priorities can be decided by comparing the second (or even third) atom of the respective group.



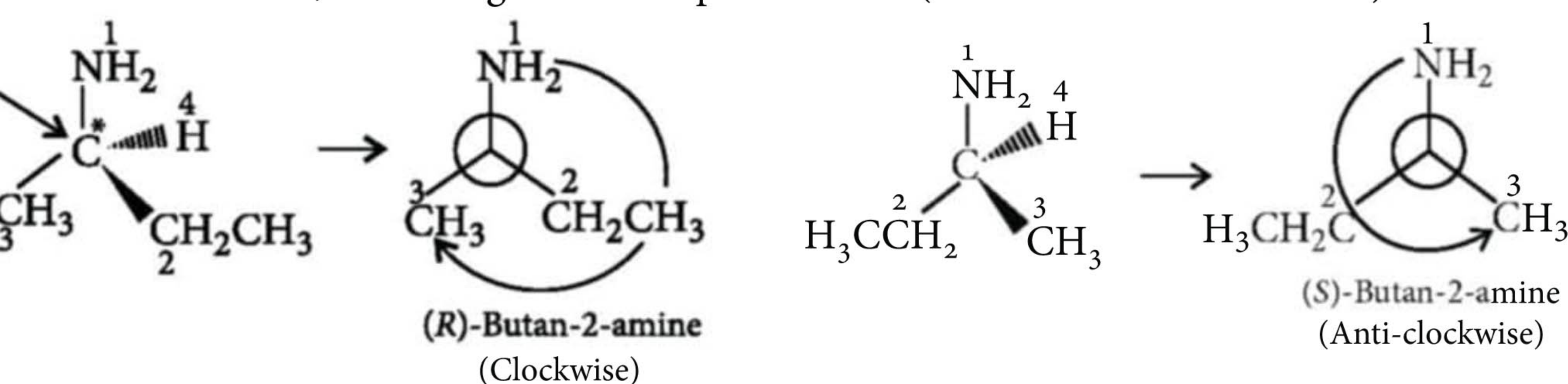
3 : This is an extension of rule II. If the second atoms are attached by double bond or triple bond, then double bonds are treated as they have two single bonds and triple bonds as they have three single bonds *i.e.*,



Thus, priority order is $\text{C}_6\text{H}_5 > -\text{C}\equiv\text{CH} > -\text{CH}=\text{CH}_2 > -\text{CH}(\text{CH}_3)_2$

STEP II

For deciding the priority of four atoms or groups attached to the chirality centre, the molecule (formula) is now rotated so that the group of lowest priority (4) is directed away from the eye (viewer). The arrangement of remaining three groups is viewed in decreasing order of their priorities, *i.e.*, from 1 to 2 to 3. In looking so, if the eye travels in a clockwise direction, the configuration is specified as *R* (from *rectus* Latin for right), while in case if eye travels in the anticlockwise direction, the configuration is specified as *S* (from *sinister* Latin for left).



Relative Configuration

The configuration of the (OH) group at penultimate carbon of various stereoisomers are studied with respect to glyceraldehyde.

CONFIGURATION

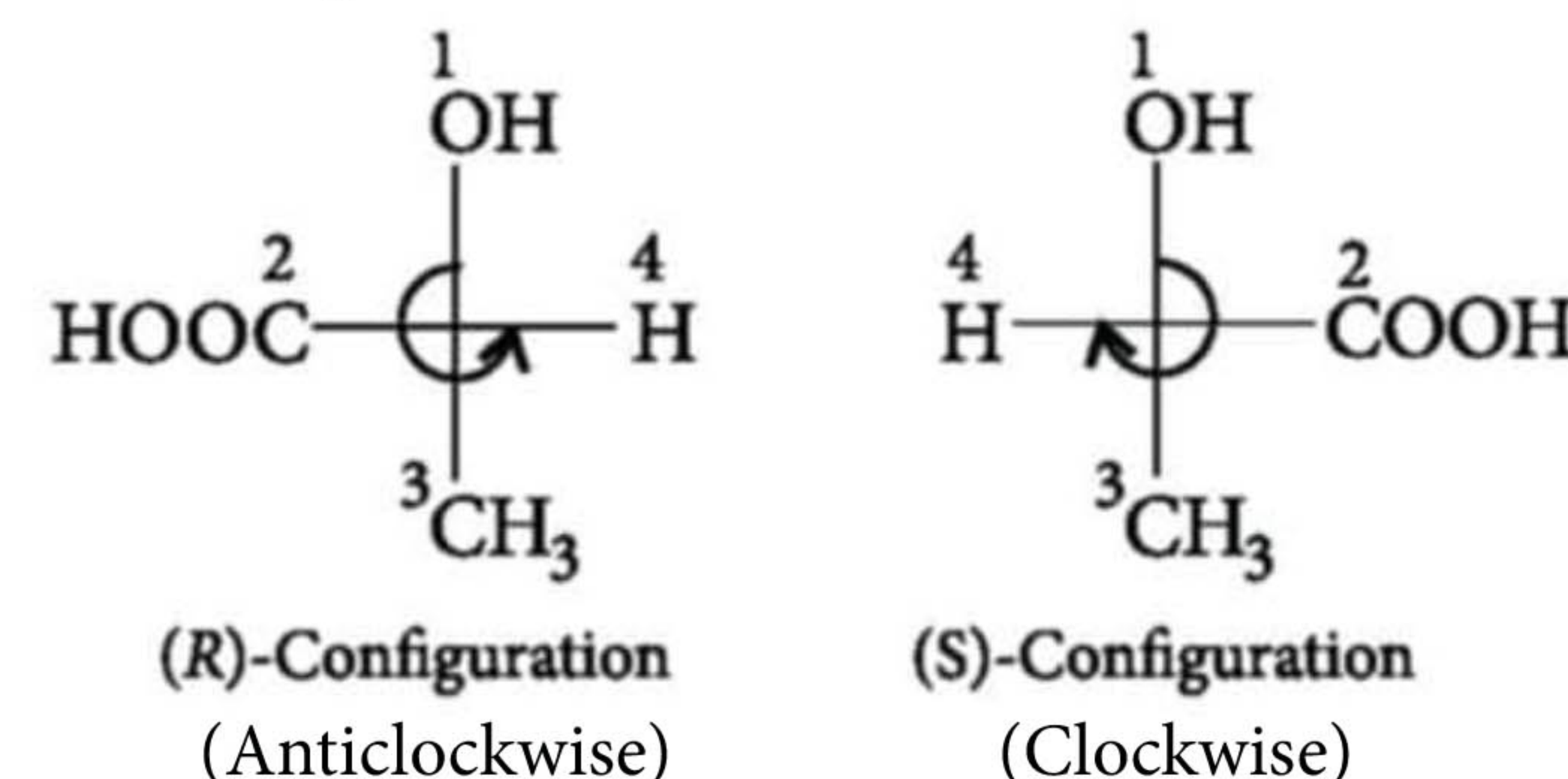
The arrangement of atoms or groups in space that characterises a stereoisomer is called its configuration. The sign of rotation of a stereoisomer is not related to its configuration.

Absolute Configuration

Cahn-Ingold-Prelog system has been developed to assign absolute configuration.

If the lowest priority group occupies horizontal position (left or right) in the Fischer projection formula, then change the configuration obtained from (*R*) to (*S*) or (*S*) to (*R*).

For example,

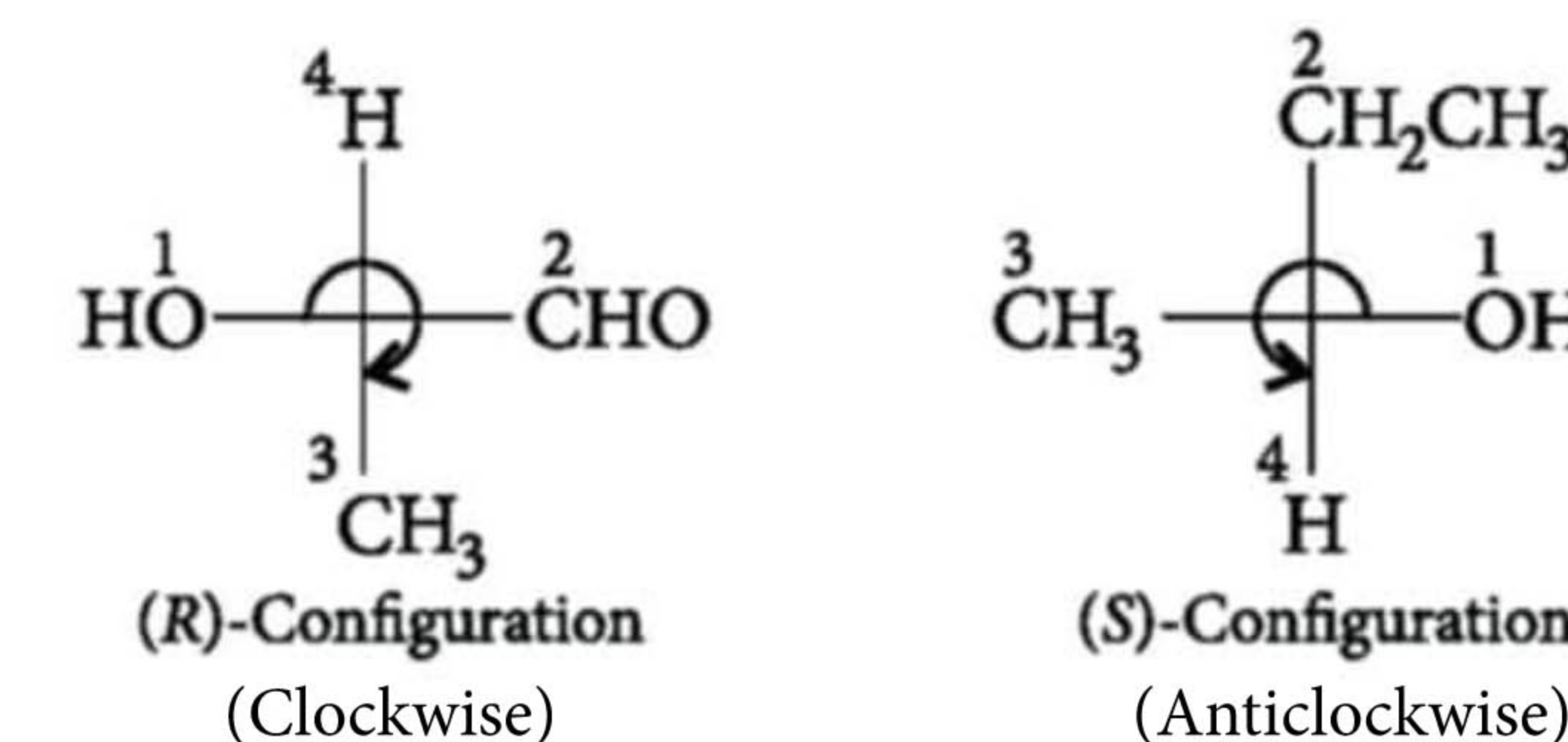


Golden Rule

Assigning *R, S* Configuration in Fischer Projection

- When atom or group of lowest priority is at the bottom of vertical line :

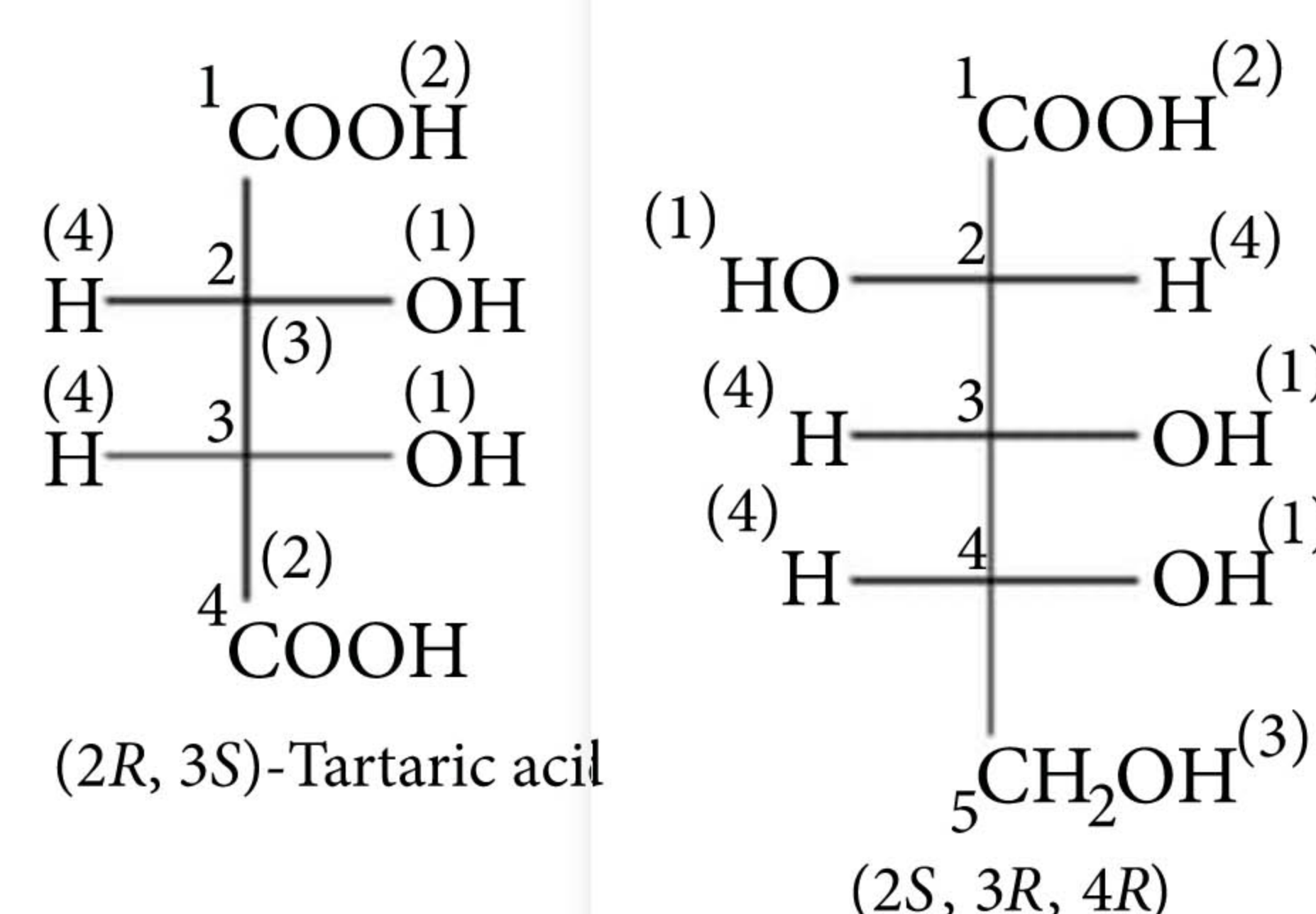
There is an easy way of assigning *R* and *S* configuration to optically active isomers represented by Fischer projection formula. Firstly assign priorities to the groups/atoms attached to chiral centre without making any change/interchange in the strength. Find out the configuration. Now if the lowest priority group occupies vertical (upward or downward) position in the original Fischer projection, then the configuration obtained above gives the actual configuration of the molecule. For example,



Assigning *R, S* configuration of the compounds with more than one chiral centres

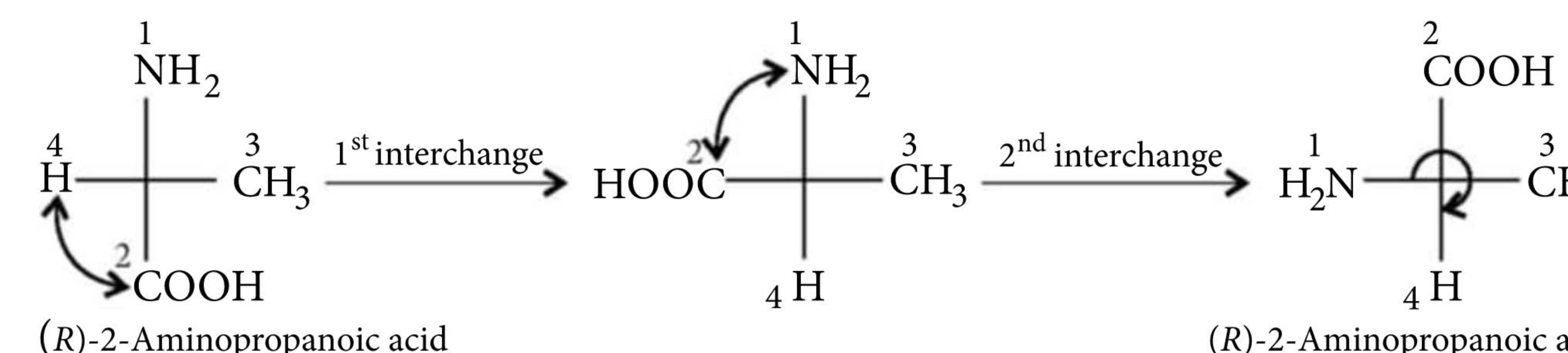
If a compound has two or more chiral carbon atoms, separate configuration is assigned to each carbon atom on the basis of sequence rule. In such compounds, application of golden rule is more convenient.

For example,



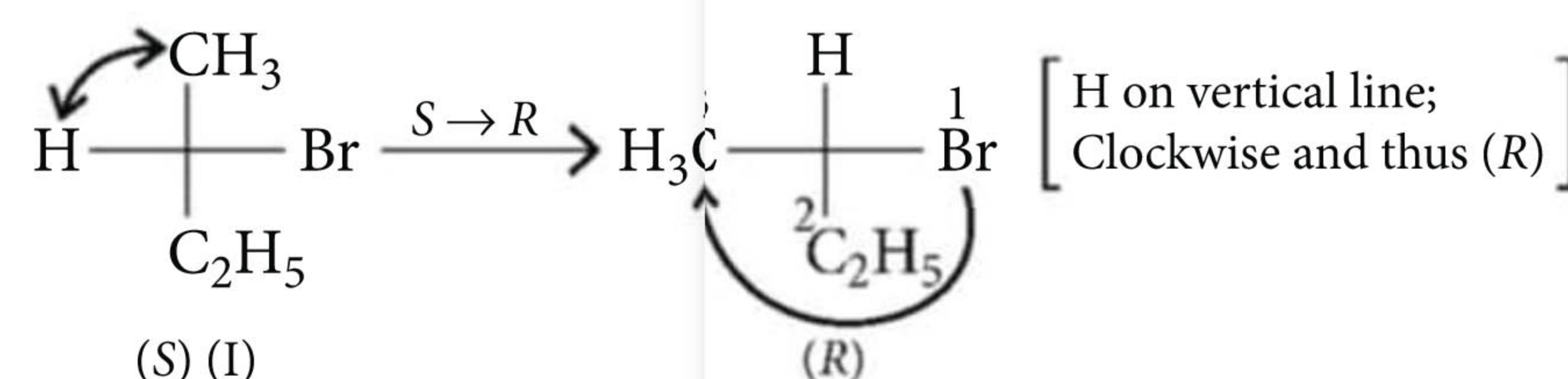
- When atom or group of lowest priority is not on the vertical line :

If the lowest priority group/atom does not lie at vertical downward or upward position (bottom or above), then make two interchanges of atoms or groups in such a way that the atom or group of lowest priority is placed either vertically upward or downward. Now, assign the configuration according to path followed in decreasing order of priority.



Effect on the configuration

- By exchanging a horizontal and vertical ligand :

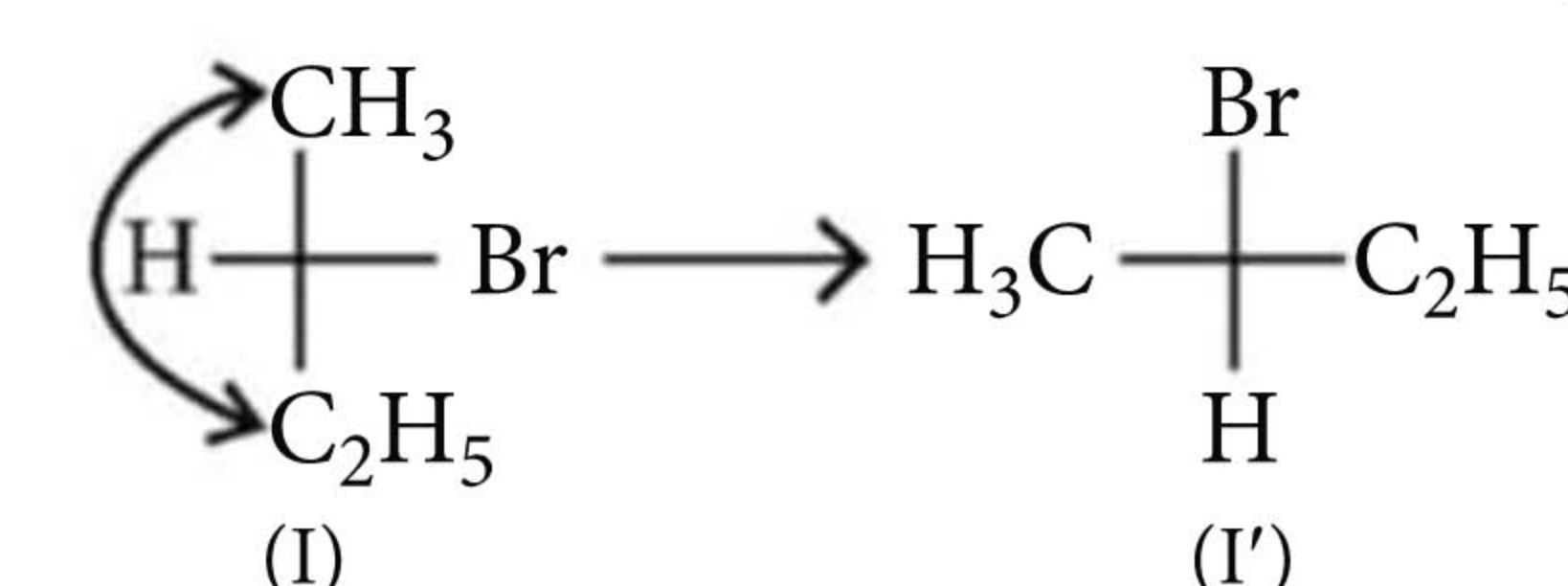


- By 180° vertical or horizontal rotation outside the plane of paper : This type of operation is not allowed in Fischer projection because any flipping out of the plane of paper (side to side or top to bottom) would change the ligands formerly projecting behind the plane of paper to projecting towards the observer.

Those ligands formerly pointing towards the observer would change to behind the paper.

- By a 90° rotation on the plane of paper :

This type of operation is also not allowed in Fischer projection. For example,

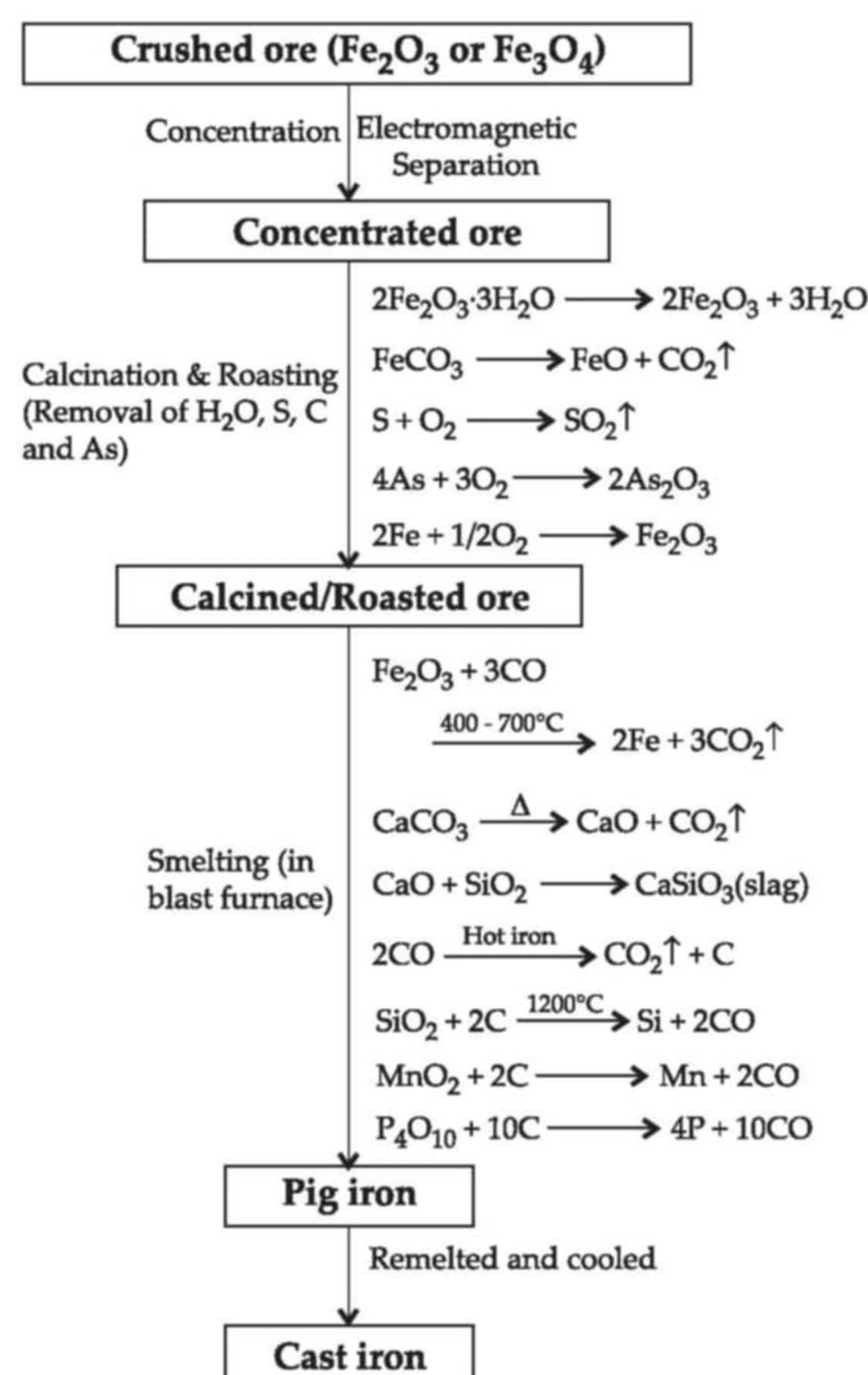


In (I), H and Br project behind the plane, but a 90° rotation on the plane does not change the projection of bonds towards or away from the observer.

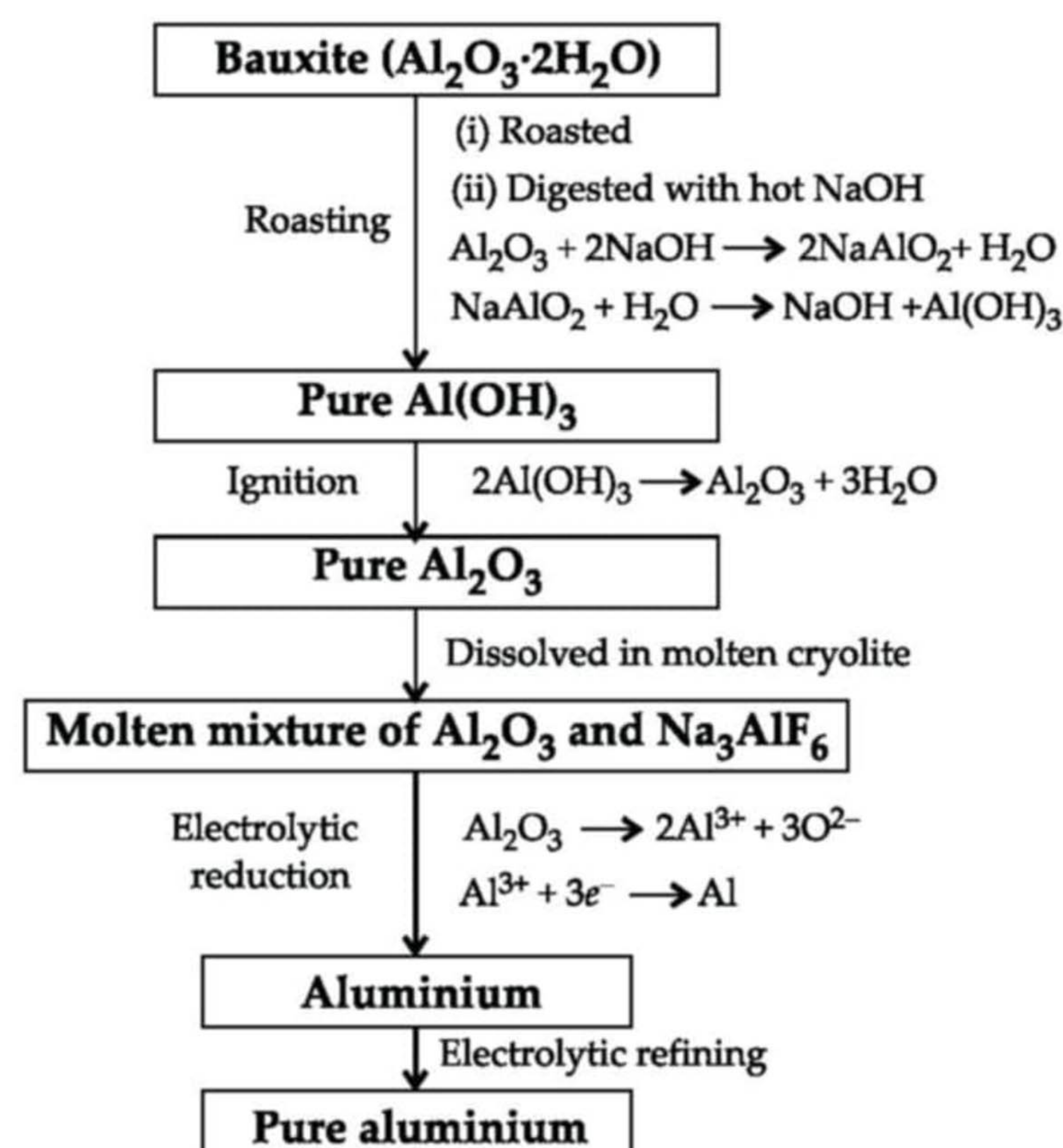
Refining of Crude Metals

S. No.	Methods	Metals purified
1.	Distillation	Zinc and mercury
2.	Electrolysis	Impure metal is made anode and the pure metal is cathode. The net result is the transfer of pure metal from anode to cathode. Copper, gold, silver, lead, zinc, aluminium
3.	Liquation	A low melting metal like tin and lead can be made to flow on a sloping surface and thus separated from higher melting impurities.
4.	Zone refining	Metals of high purity are obtained. Silicon, germanium, boron, gallium, indium are purified (which are used in semiconductors). It is based on the fact that impurities are more soluble in the melt than in the pure metal.
5.	Vapour phase refining	In Mond's process for the refining of nickel. $\text{Ni} + 4\text{CO} \xrightarrow{80^\circ\text{C}} \text{Ni}(\text{CO})_4 \xrightarrow{200^\circ\text{C}} \text{Ni} + 4\text{CO}\uparrow$ (impure) (pure) In van Arkel method for zirconium. $\text{Zr} + 2\text{I}_2 \xrightarrow{600\text{ K}} \text{ZrI}_4 \xrightarrow{1800\text{ K}} \text{Zr} + 2\text{I}_2$ (impure) (pure)

EXTRACTION OF IRON (Fe)



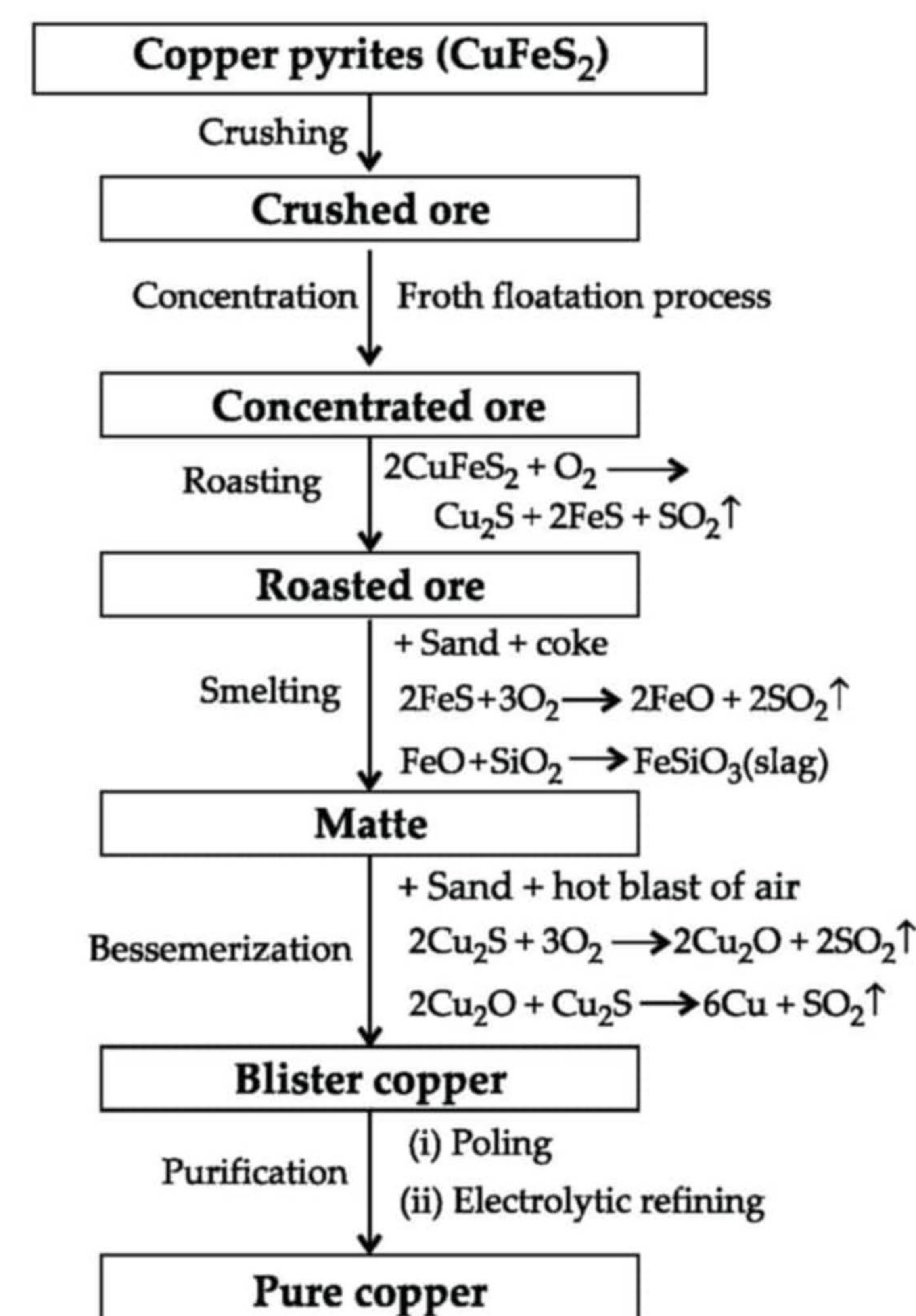
EXTRACTION OF ALUMINIUM (Al)



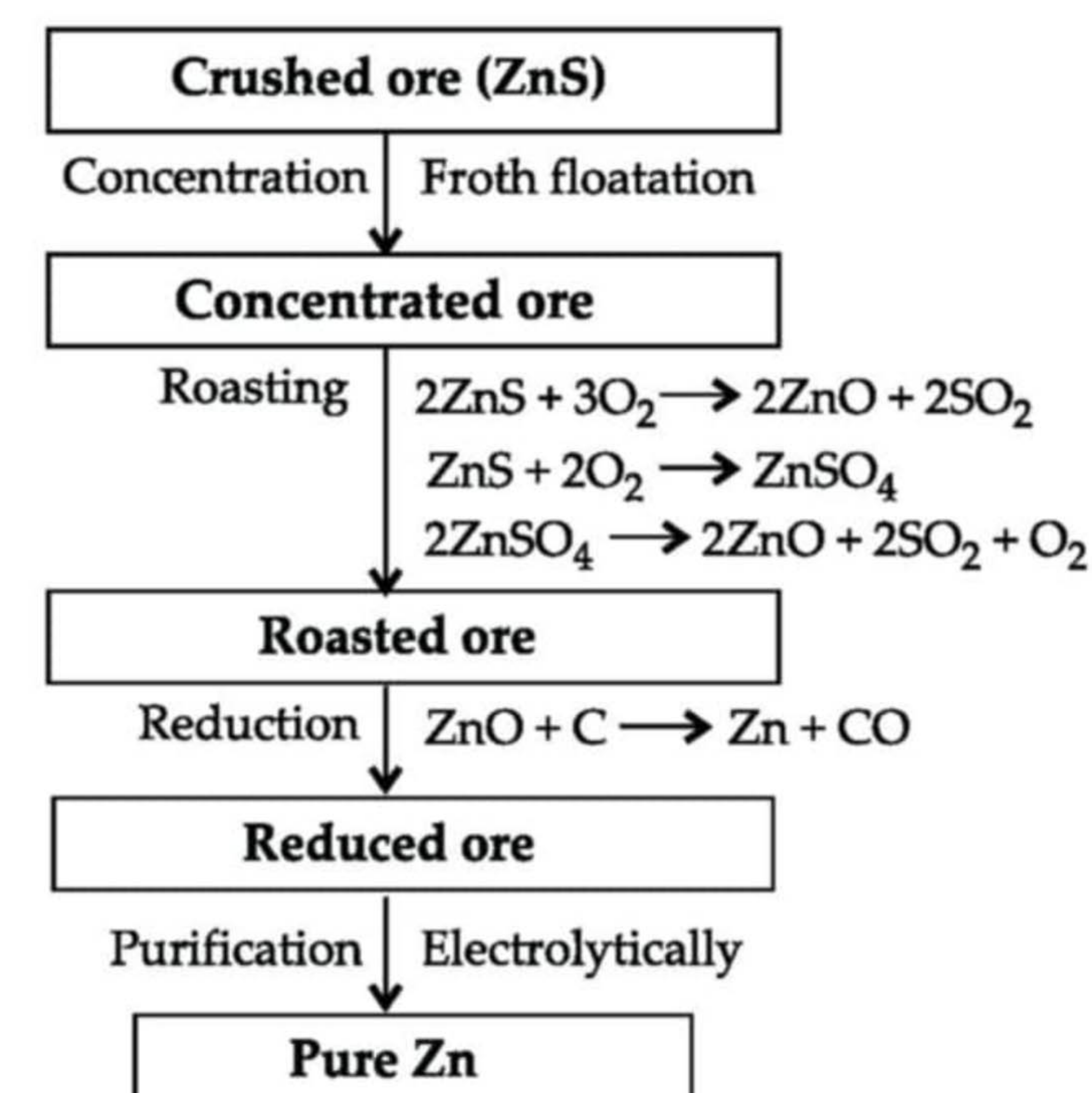
Monthly Test Drive CLASS XI ANSWER KEY

- | | | | | |
|-----------|-----------|-------------|---------|-----------|
| 1. (a) | 2. (d) | 3. (c) | 4. (a) | 5. (b) |
| 6. (a) | 7. (b) | 8. (b) | 9. (a) | 10. (c) |
| 11. (d) | 12. (c) | 13. (a) | 14. (a) | 15. (d) |
| 16. (b) | 17. (b) | 18. (a) | 19. (b) | 20. (b,c) |
| 21. (a,b) | 22. (a,c) | 23. (a,c,d) | 24. (5) | 25. (5) |
| 26. (3) | 27. (c) | 28. (a) | 29. (b) | 30. (d) |

EXTRACTION OF COPPER (Cu)



EXTRACTION OF ZINC (Zn)



PEEP INTO PREVIOUS YEARS

4. Match the refining methods (Column I) with metals (Column II).

Column I (Refining methods)	Column II (Metals)
(I) Liquation	(a) Zr
(II) Zone refining	(b) Ni
(III) Mond process	(c) Sn
(IV) van Arkel method	(d) Ga
(a) (I) - (c); (II) - (a); (III) - (b); (IV) - (d)	
(b) (I) - (b); (II) - (c); (III) - (d); (IV) - (a)	
(c) (I) - (b); (II) - (d); (III) - (a); (IV) - (c)	
(d) (I) - (c); (II) - (d); (III) - (b); (IV) - (a)	

(JEE Main 2019)

5. Considering Ellingham diagram, which of the following metals can be used to reduce alumina?

(a) Fe (b) Zn (c) Mg (d) Cu

(NEET 2018)

POINTS FOR EXTRA SCORING

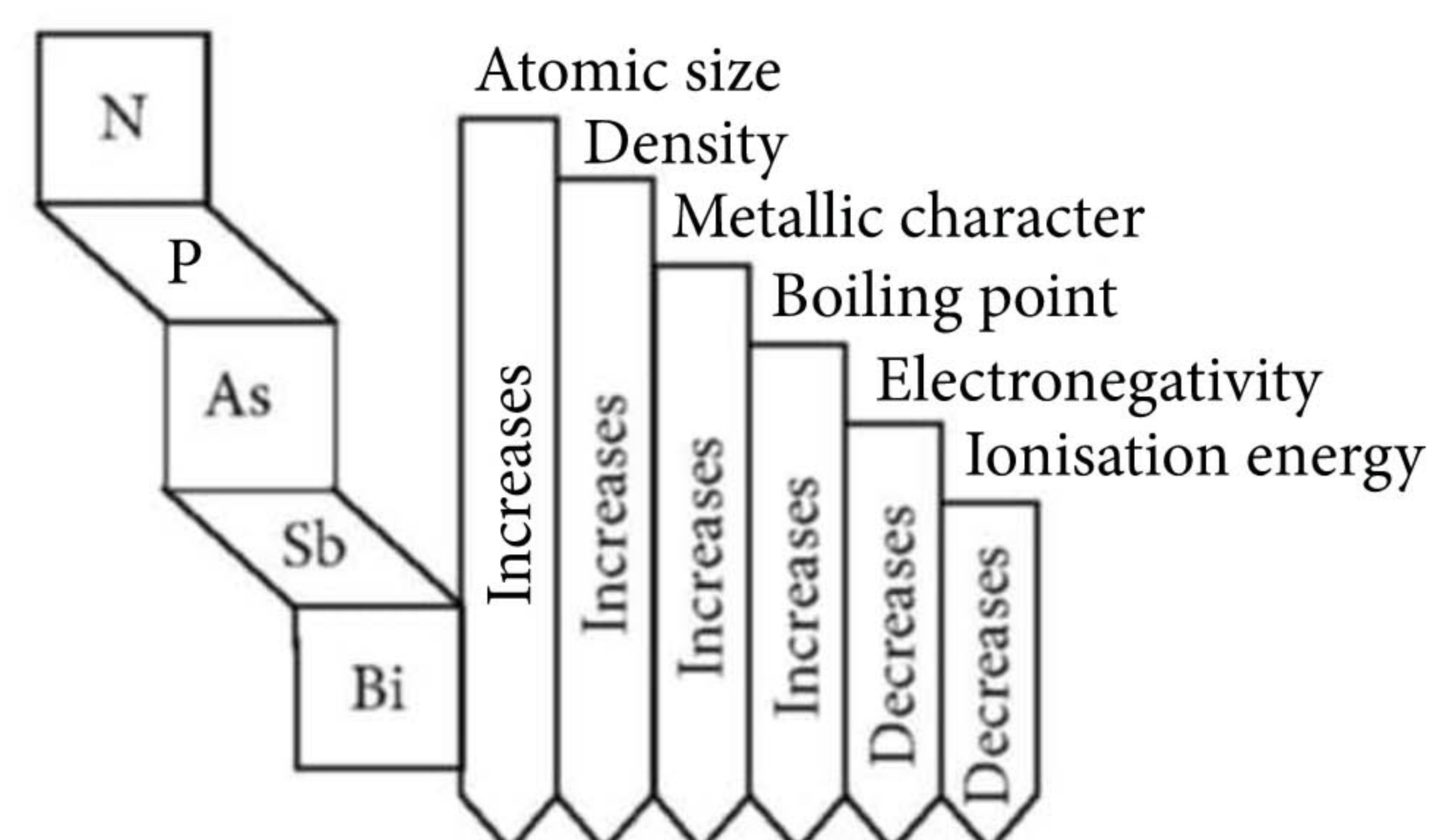
- **Refractory material** : These are the substances which bear very high temperature without melting and becoming soft. Hence, the furnace is lined with refractory material.
- **Pyrometallurgy** : The process of extraction of metals using heat is called pyrometallurgy. It involves roasting, calcination, smelting, reduction and refining of metals from sulphide, carbonate, oxide ores, etc.
- **Pickling** : The process of removing layers of basic oxides from metal surfaces before electroplating is called pickling.
- **Slagging** : The removal of impurities from a mineral by forming molten salts is called slagging.
- **Anodising** : The process of producing an oxide coating on a metallic surface by making it the anode in an electrolytic bath during electrolysis is called anodising.
- **Amalgamation** : The process of combining metals present in their native ores with mercury to form alloys (amalgams) is called amalgamation. This process is applicable in the extraction of noble metals like Au and Ag.
- **Pulverisation** : The process of grinding the crushed ore into fine powder is called pulverisation.

The *p*-Block Elements (Group 15 to 18)

GROUP 15 ELEMENTS (NITROGEN FAMILY)

- Group 15 of the periodic table consists of six elements viz. nitrogen (N), phosphorus (P), arsenic (As), antimony (Sb), bismuth (Bi) and Moscovium (Mc)
- Electronic configuration :** The electronic configuration of these elements is ns^2np^3 .

General Trends in Physical Properties



Chemical Properties

- Hydrides :** Form MH_3 type hydrides.
 - Melting point :** $PH_3 < AsH_3 < SbH_3 < NH_3$
 - Boiling point :** $BiH_3 > SbH_3 > NH_3 > AsH_3 > PH_3$

Stability, Basic character, Bond angle, Strength of $M-H$ bond decrease.

NH_3 , PH_3 , AsH_3 , SbH_3 , BiH_3
Bond angle : (107.8°) (93.6°) (91.8°) (91.3°) (90.0°)

Reducing character, Acidic character, Poisonous character increase.

- Halides :** Nitrogen forms MX_3 type of halides while rest other form both MX_3 and MX_5 types of halides.

Property	Gradation	Reason
Stability of trihalides of nitrogen	$NF_3 > NCl_3 > NBr_3$	Large size difference between N and the halogens
Lewis acid strength	$PCl_3 > AsCl_3 > SbCl_3$	$PF_3 > PBr_3 > PI_3$
Bond angle among the halides of phosphorus	$PF_3 < PCl_3 < PBr_3 < PI_3$	Due to decreased bond pair-bond pair repulsion as these move away from P due to increased electronegativity of X

- Oxides :** All the elements of this group form oxides, of the type M_2O_3 , M_2O_4 and M_2O_5 .

Property	Gradation	Reason
Acidic strength of trioxides	$N_2O_3 > P_2O_3 > As_2O_3$	Electronegativity of central atom decreases
Acidic strength of oxides of nitrogen	$N_2O < NO < N_2O_3 < N_2O_4 < N_2O_5$	Oxidation state of central atom increases
Thermal stability of pentoxide	$P_2O_5 > As_2O_5 > Sb_2O_5 > N_2O_5 > Bi_2O_5$	Stability of oxides of a higher oxidation state i.e., M_2O_5 decreases with increasing atomic number

Anomalous Behaviour of Nitrogen

- Small size.
- High electronegativity.
- Absence of *d*-orbitals in the valence shell.
- Tendency to form multiple bonds.

The main points of difference are :

- Nitrogen is a gas while other members are solids.
- Nitrogen exists as diatomic molecule while other elements except bismuth form tetra-atomic molecules such as P_4 , As_4 and Sb_4 .
- The catenation property is more pronounced in nitrogen. Chains containing upto eight nitrogen atoms are known but in other elements catenation is limited to two atoms only.
- Nitrogen does not form pentahalides.
- Nitrogen exhibits a large number of oxidation states from -3 to +5 i.e., +5, +4, +3, +2, +1, 0, -1, -2 and -3.

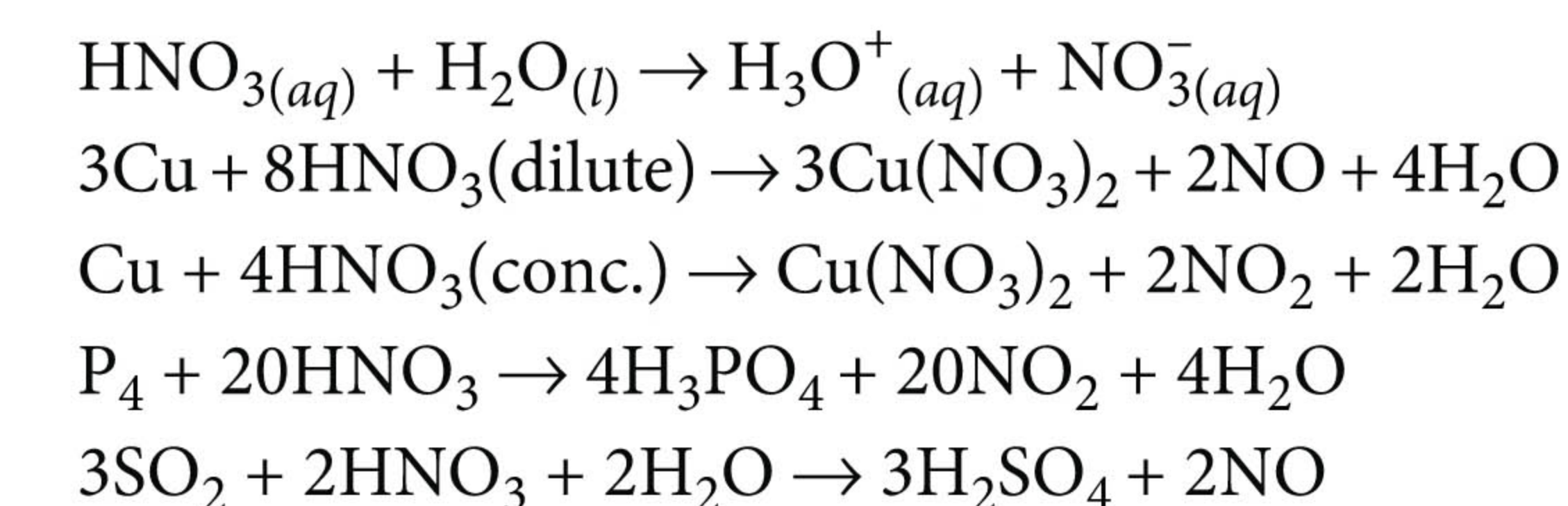
Ammonia (NH_3)

- Preparation :**
 - $2NH_4Cl + Ca(OH)_2 \xrightarrow{\Delta} CaCl_2 + 2NH_3 + 2H_2O$
 - Manufacture (Haber's Process) :
 $N_2 + 3H_2 \xrightarrow[200-300 \text{ atm}]{Fe + Mo, 750 \text{ K}} 2NH_3 + 24 \text{ kcal}$
- Physical Properties :**
 - It is a colourless, pungent smelling gas which brings tears to the eyes.

- It is lighter than air and highly soluble in water due to formation of hydrogen bonds.
- Chemical Properties :**
 - It forms salts with mineral acids.
 $NH_3 + HCl \longrightarrow NH_4Cl$
 $2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$
 - It ionises partially in water yielding a weakly basic solution.
 $NH_3 + H_2O \longrightarrow NH_4OH \rightleftharpoons NH_4^+ + OH^-$

Nitric Acid (HNO_3)

- Preparation :**
 - Laboratory preparation :**
 $2KNO_3 + H_2SO_4 \longrightarrow 2HNO_3 + K_2SO_4$
 - Ostwald's process :**
 $4NH_3 + 5O_2 \xrightarrow{Pt \text{ gauze, } 1075 \text{ K}} 4NO + 6H_2O$
 $2NO + O_2 \rightleftharpoons 2NO_2$
 $3NO_2 + H_2O \longrightarrow 2HNO_3 + NO$
- Physical Properties :**
 - Anhydrous acid is a colourless, fuming liquid with a pungent smell, soluble in water in all proportions.
 - Aqueous solution containing 68% HNO_3 forms an azeotropic mixture.
- Chemical Properties :** It is a very strong acid and very strong oxidizing agent as it decomposes to give nascent oxygen easily.



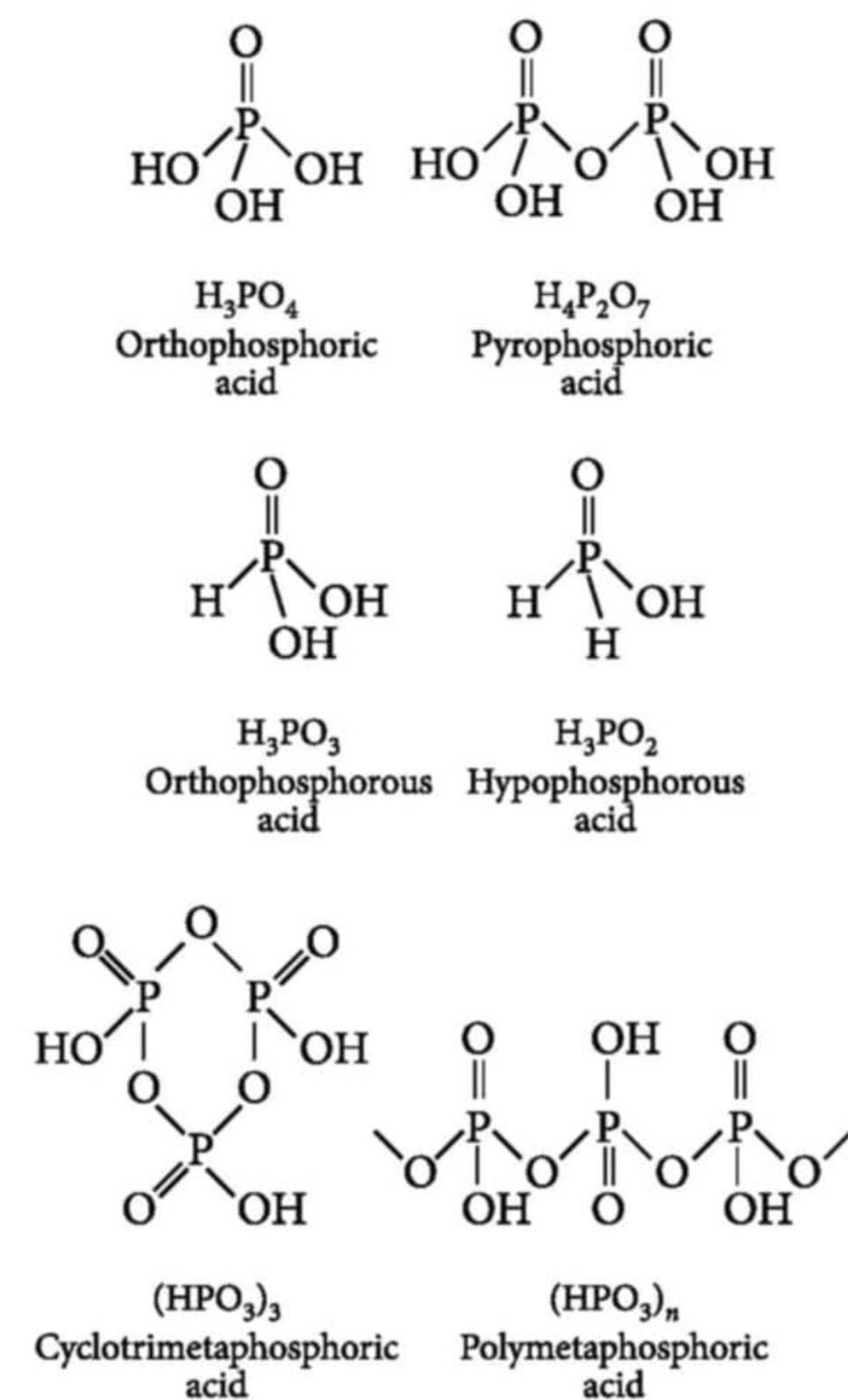
Oxides of Nitrogen

Oxides	O.S. of N	Physical appearance	Structure
N_2O Nitrous oxide	+1	Colourless gas	$N \equiv N \rightarrow O$
NO Nitric oxide	+2	Colourless gas	$N=O$
N_2O_3 Dinitrogen trioxide	+3	Blue coloured solid	$O=N-N=O$
N_2O_4 Dinitrogen tetraoxide	+4	Colourless solid	$O=N-N=O$
NO_2 Nitrogen dioxide	+4	Brown gas	$O=N \rightarrow O$
N_2O_5 Dinitrogen pentaoxide	+5	Colourless gas	$O=N-O-N=O$

Some Important Compounds of Phosphorus

Compound	Preparation	Properties	Uses
PH_3 	$Ca_3P_2 + 6H_2O \rightarrow 3Ca(OH)_2 + 2PH_3$ $Ca_3P_2 + 6HCl \rightarrow 3CaCl_2 + 2PH_3$ $P_4 + 3NaOH + 3H_2O \rightarrow PH_3 + 3NaH_2PO_2$ (sodium hypophosphite) $PH_4I + KOH \rightarrow KI + H_2O + PH_3$	$3CuSO_4 + 2PH_3 \rightarrow Cu_3P_2 + 3H_2SO_4$ $3HgCl_2 + 2PH_3 \rightarrow Hg_3P_2 + 6HCl$ $PH_3 + HBr \rightarrow PH_4Br$ $PH_3 + 4O_2 \rightarrow P_2O_5 + 3H_2O$ $PH_3 + 16HNO_3 \rightarrow P_2O_5 + 16NO_2 + 11H_2O$	Used in smoke screens and Holme's signals.
PCl_5 	$P_4 + 10Cl_2 \rightarrow 4PCl_5$ (white or red) $P_4 + 10SO_2Cl_2 \rightarrow 4PCl_5 + 10SO_2$	$PCl_5 + 4H_2O (\text{excess}) \rightarrow H_3PO_4 + 5HCl$ $PCl_5 + SO_2 \rightarrow SOCl_2 + POCl_3$ $6PCl_5 + P_4O_{10} \rightarrow 10POCl_3$ $PCl_5 + Zn \rightarrow ZnCl_2 + PCl_3$	Used as chlorinating and dehydrating agent.
PCl_3 	$P_4 + 6Cl_2 \rightarrow 4PCl_3$ $P_4 + 8SOCl_2 \rightarrow 4PCl_3 + 4SO_2 + 2S_2Cl_2$	$PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$ $3CH_3COOH + PCl_3 \rightarrow 3CH_3COCl + H_3PO_3$ $3C_2H_5OH + PCl_3 \rightarrow 3C_2H_5Cl + H_3PO_3$	Used as reagent in organic synthesis and as a precursor of PCl_5 , $POCl_3$ and $PSCl_3$.

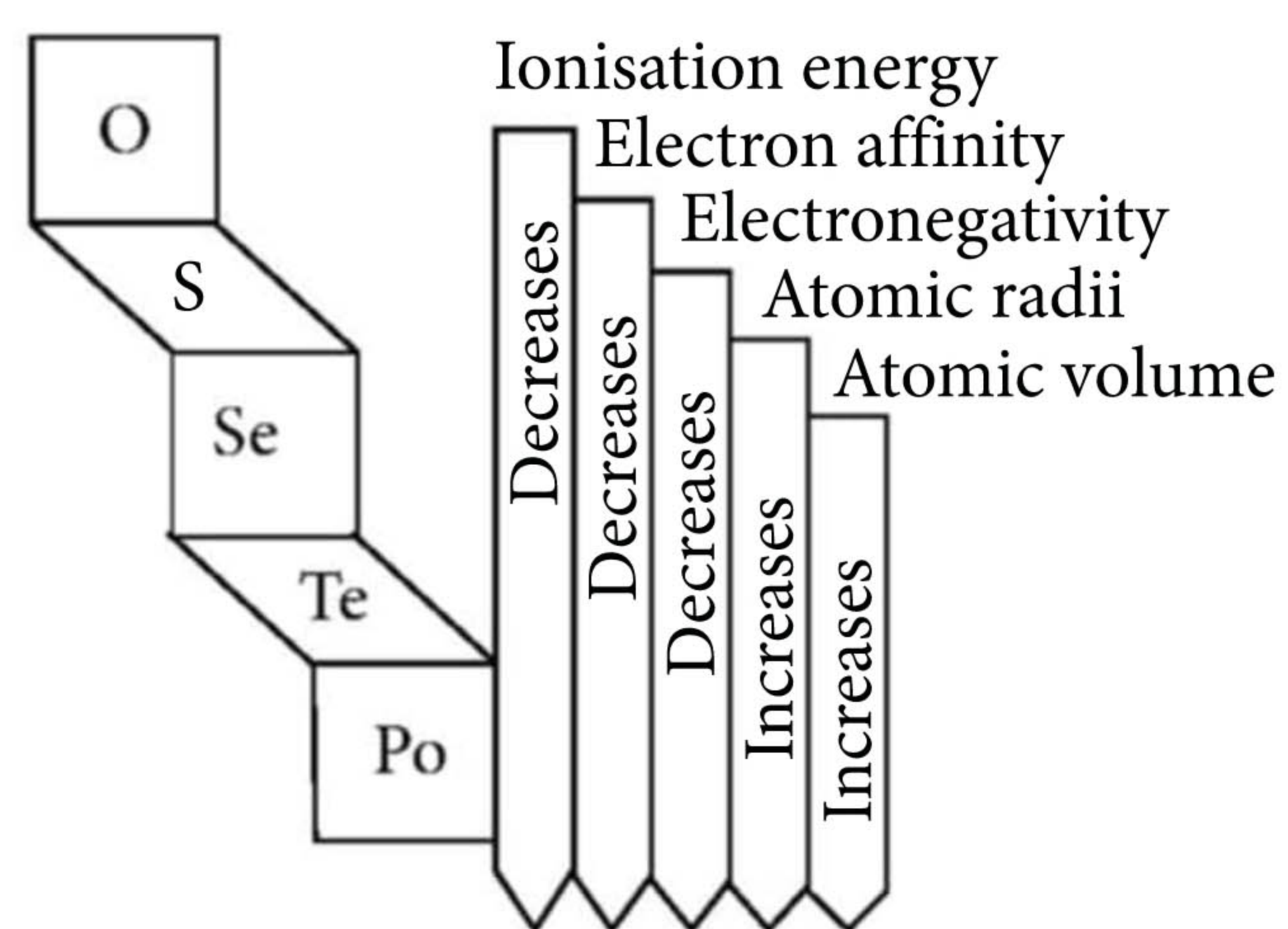
Oxoacids of Phosphorus



GROUP 16 ELEMENTS (OXYGEN FAMILY)

- The elements oxygen (O), sulphur (S), Selenium (Se), tellurium (Te) and polonium (Po) constitute group 16 of the periodic table.
- Electronic configuration :** Their valence shell electronic configuration is ns^2np^4 where $n = 2$ to 6.

General Trends in Physical Properties



Chemical Properties

- Hydrides :** All the elements form stable hydrides of the type H_2M , where M is sp^3 hybridised.
 H_2O , H_2S , H_2Se , H_2Te
 Stability decreases
 Poisonous nature, acidic character, reducing character increase
- Halides :** Form MX_6 , MX_4 and MX_2 types of halides :
 - Dihalides :** All elements except selenium form dihalides.
 - Tetrahalides :** SF_4 (gas), SeF_4 (liquid), TeF_4 (solid). SF_4 is readily hydrolysed than SF_6 .
- Oxides :** Form MO , MO_2 and MO_3 types oxides.

Anomalous Behaviour of Oxygen

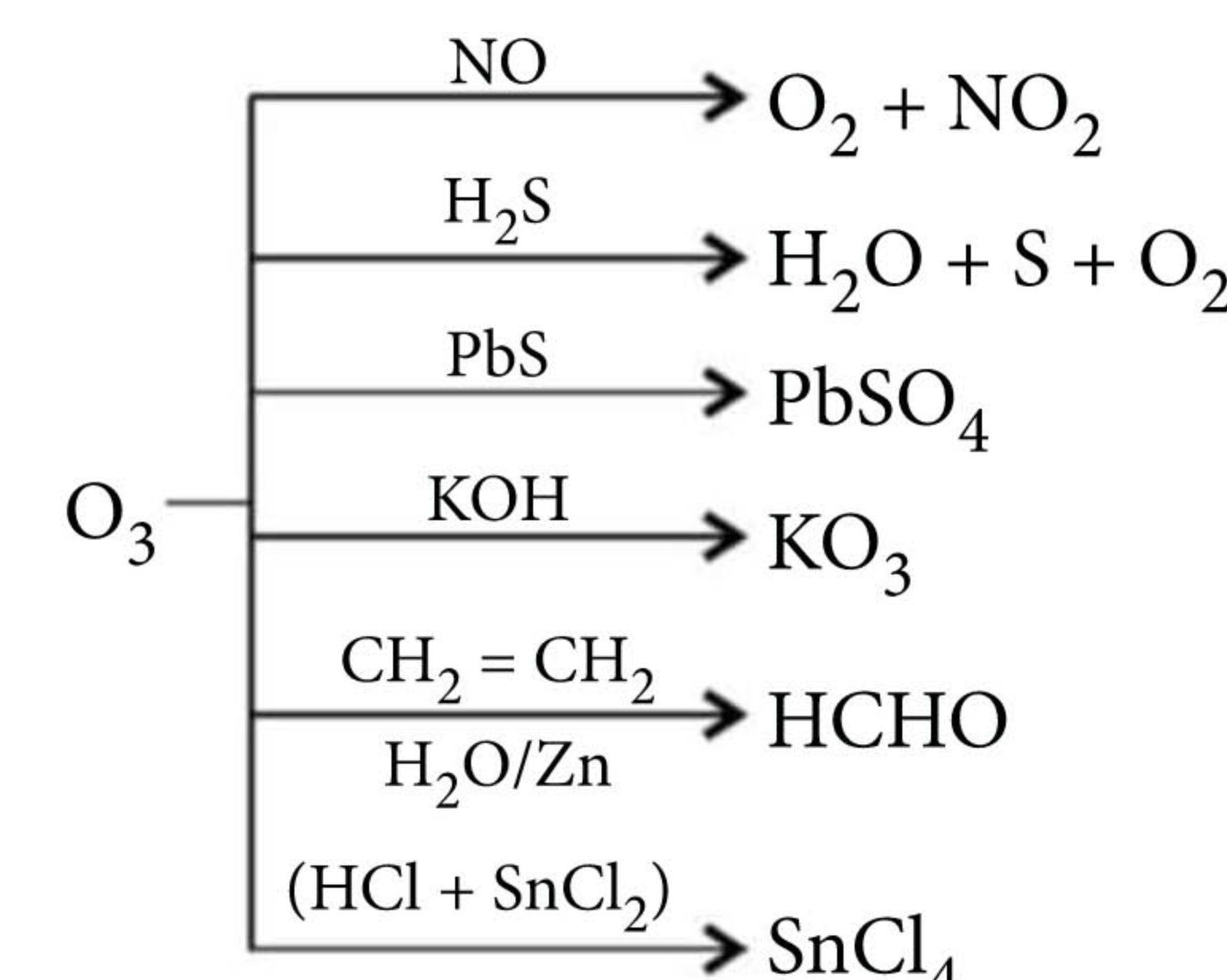
- Oxygen is a diatomic gas while others are solids.
- Oxygen exhibits oxidation states of -2 , -1 and $+2$ only while other members show both negative and positive oxidation states like -2 , $+2$, $+4$ and $+6$.
- Due to high electronegativity of oxygen, hydrogen bonding is present in water.
- Oxygen is highly non-metallic due to high value of electronegativity.
- Oxygen is paramagnetic while others are diamagnetic.

Dioxygen (O_2)

- Laboratory preparation :**
 $2\text{Na}_2\text{O}_2(\text{s}) + 2\text{H}_2\text{O}(\text{l}) \longrightarrow 4\text{NaOH}(\text{aq}) + \text{O}_2(\text{g})$
 $2\text{KClO}_3 \xrightarrow[\text{MnO}_2]{\Delta} 2\text{KCl} + 3\text{O}_2$
- Physical Properties :**
 - It is a colourless, odourless and tasteless gas. However liquid oxygen has a pale colour.
 - It exists as diatomic molecule (O_2).
- Chemical Properties :**
 O_2 is not very active under ordinary conduction as its bond dissociation energy is high. It only reacts at high temperature, but once the reaction starts it continues of its own as the combination of oxygen is always exothermic.
 $2\text{Mg} + \text{O}_2 \longrightarrow 2\text{MgO}$; $4\text{P} + 5\text{O}_2 \longrightarrow 2\text{P}_2\text{O}_5$
 $4\text{Al} + 3\text{O}_2 \longrightarrow 2\text{Al}_2\text{O}_3$; $2\text{NO} + \text{O}_2 \longrightarrow 2\text{NO}_2$
 $4\text{HCl} + \text{O}_2 \xrightarrow[\text{CuCl}_2]{700\text{ K}} 2\text{H}_2\text{O} + \text{Cl}_2$
- Uses**
 - For artificial respiration in hospitals and by mountaineers, pilots and divers.
 - Liquid dioxygen is used as a rocket fuel.

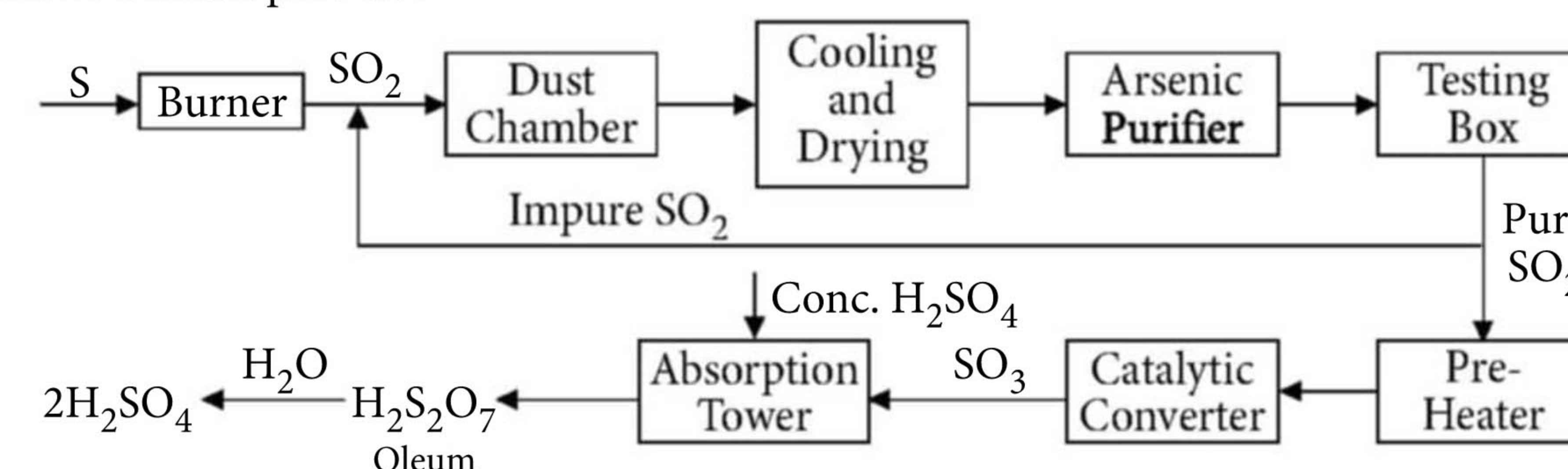
Ozone (O_3)

- Pale blue gas with characteristic strong smell, slightly soluble in water but more soluble in turpentine oil, glacial acetic acid and CCl_4 .



Sulphuric Acid (H_2SO_4)

- Preparation :** Contact process :



Structure	Properties	Uses
<p>Sulphuric acid Sulphate ion</p>	H_2SO_4 <ul style="list-style-type: none"> $\xrightarrow{\text{NaOH}}$ $\text{NaHSO}_4 + \text{H}_2\text{O}$ $\xrightarrow{\text{NaHCO}_3}$ $\text{Na}_2\text{SO}_4 + \text{CO}_2 + \text{H}_2\text{O}$ $\xrightarrow{\text{Zn}}$ $\text{ZnSO}_4 + \text{H}_2$ $\xrightarrow{\text{C}_{12}\text{H}_{22}\text{O}_{11}}$ $12\text{C} + 11\text{H}_2\text{O}$ $\xrightarrow{\text{S}_8}$ $\text{SO}_2 + \text{H}_2\text{O}$ $\xrightarrow{\text{Na}_2\text{S}}$ $\text{Na}_2\text{SO}_4 + \text{H}_2\text{S}$ $\xrightarrow{\text{BaCl}_2}$ $\text{BaSO}_4 + 2\text{HCl}$ $\xrightarrow{\text{K}_4[\text{Fe}(\text{CN})_6]}$ $\text{K}_2\text{SO}_4 + \text{FeSO}_4 + (\text{NH}_4)_2\text{SO}_4 + \text{CO}\uparrow$ 	It is used as oxidising agent, dehydrating agent and for the preparation of dyes, drugs, explosives, volatile acids, etc.

PEEP INTO PREVIOUS YEARS

- The species analogous to paramagnetic behaviour like O_2 is
 - monoclinic sulphur
 - rhombic sulphur
 - colloidal sulphur
 - gaseous sulphur.
 (AMU(Engg.) 2019)
- The number of $\text{S}=\text{O}$ and $\text{S}-\text{OH}$ bonds present in peroxodisulphuric acid and pyrosulphuric acid respectively are

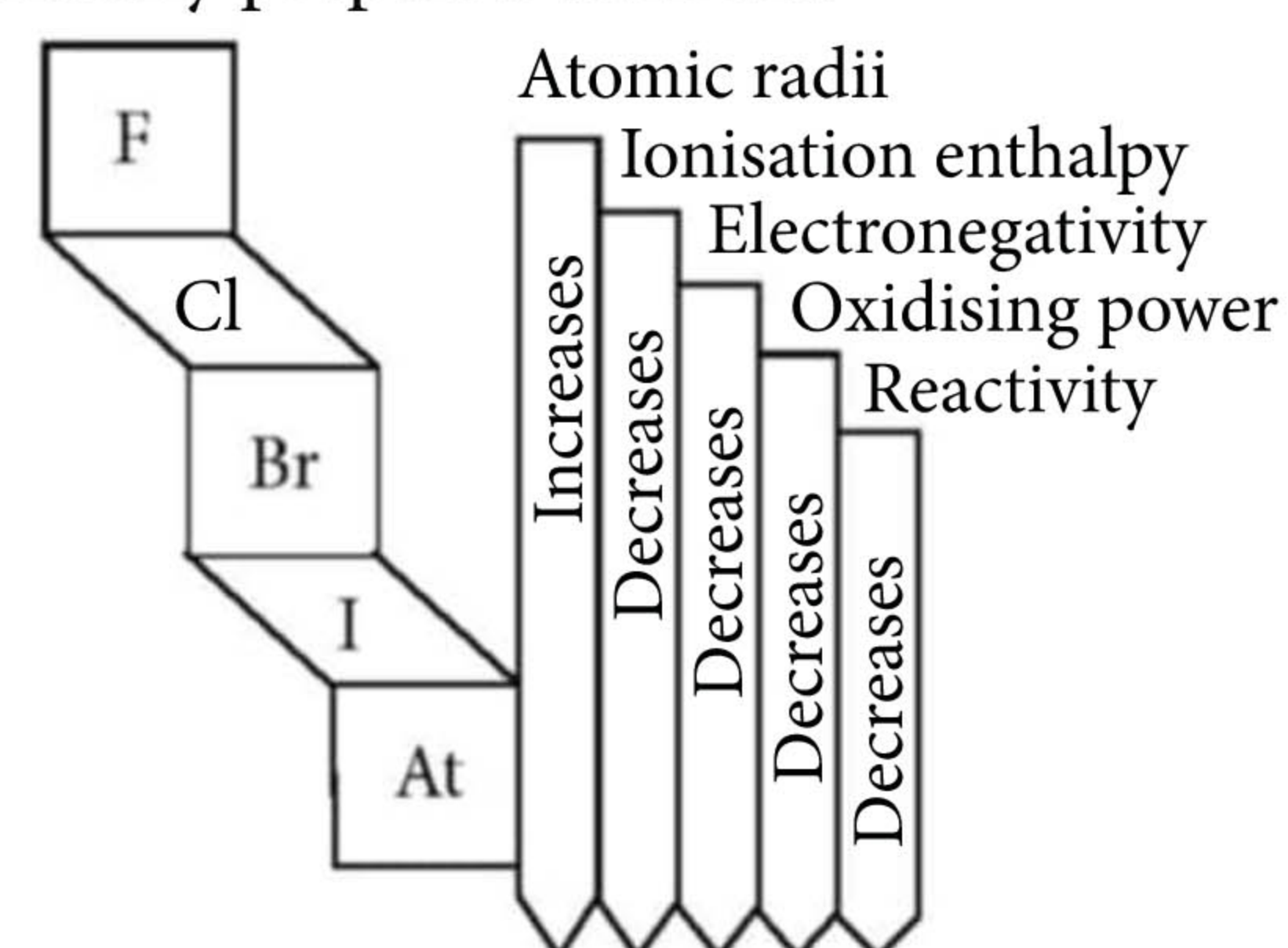
- (4 and 2) and (4 and 2)
 - (2 and 4) and (2 and 4)
 - (4 and 2) and (2 and 4)
 - (2 and 2) and (2 and 2).
- (JEE Main 2017)
- When copper is heated with conc. HNO_3 it produces
 - $\text{Cu}(\text{NO}_3)_2$, NO and NO_2
 - $\text{Cu}(\text{NO}_3)_2$ and N_2O
 - $\text{Cu}(\text{NO}_3)_2$ and NO_2
 - $\text{Cu}(\text{NO}_3)_2$ and NO
 (NEET-I 2016)

GROUP 17 ELEMENTS (HALOGEN FAMILY)

- Group 17 of the periodic table consists of fluorine (F), chlorine (Cl), bromine (Br), iodine (I), astatine (At) and Tennessine (Ts).
- General electronic configuration :** $ns^2 np^5$

General Trends in Physical Properties

- They are collectively known as halogens (sea salt forming elements). Astatine is radioactive and artificially prepared element.



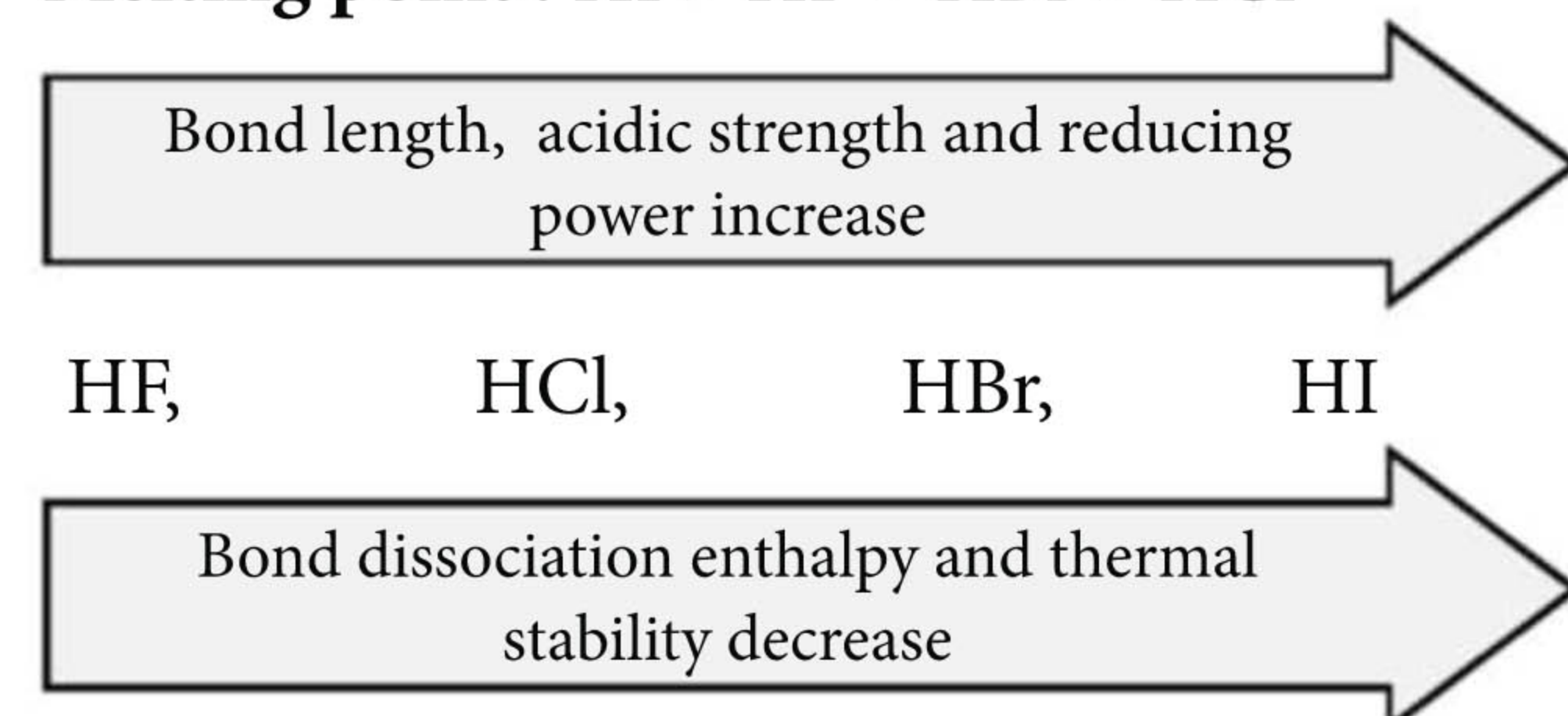
- Bond energy :** $\text{Cl}_2 > \text{Br}_2 > \text{F}_2 > \text{I}_2$
- Electron gain enthalpy :** $\text{Cl} > \text{F} > \text{Br} > \text{I}$

Chemical Properties

- Hydrogen halides :**

Boiling Point : $\text{HF} > \text{HI} > \text{HBr} > \text{HCl}$

Melting point : $\text{HI} > \text{HF} > \text{HBr} > \text{HCl}$

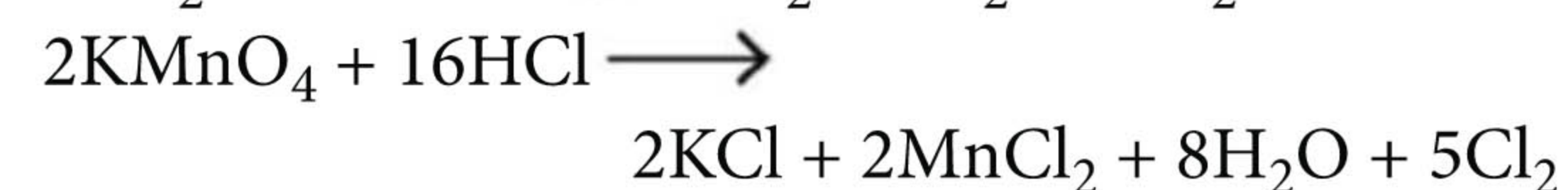
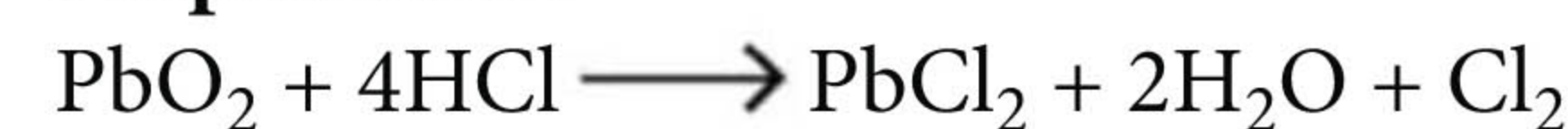


Anomalous Behaviour of Fluorine

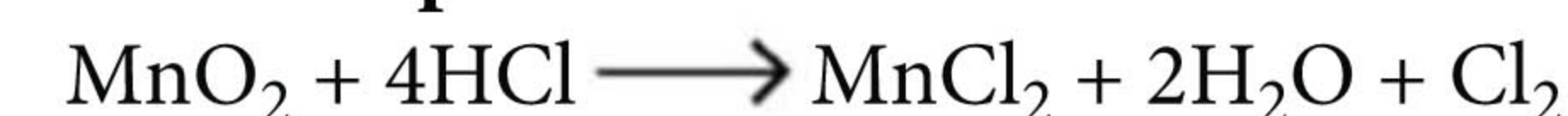
- Fluorine is most reactive of all the halogens due to low dissociation energy of F – F bond.
- It exhibits only –1 oxidation state while other members show oxidation state from –1 to +7.
- Fluorine shows H-bonding whereas other halogens do not.
- Fluorine shows a covalency of one only due to absence of d -orbital, on the other hand other halogen members can show a maximum covalency of 7.
- HF is the weakest acid of all halogen acids.
- Fluorine has the highest tendency for ionic compound formation due to high electronegativity.

Chlorine (Cl_2)

- Preparation :**



- Weldon's process :**



- Properties :**

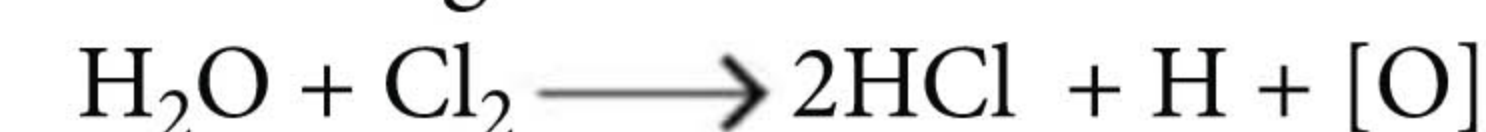
It is a yellowish green poisonous gas, soluble in water, its aqueous solution is known as chlorine water.



(hot & conc.)

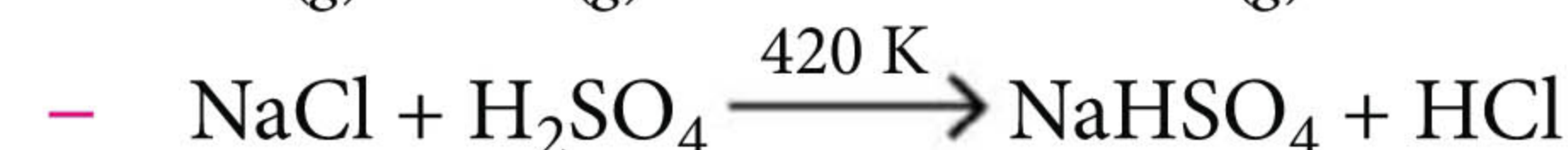
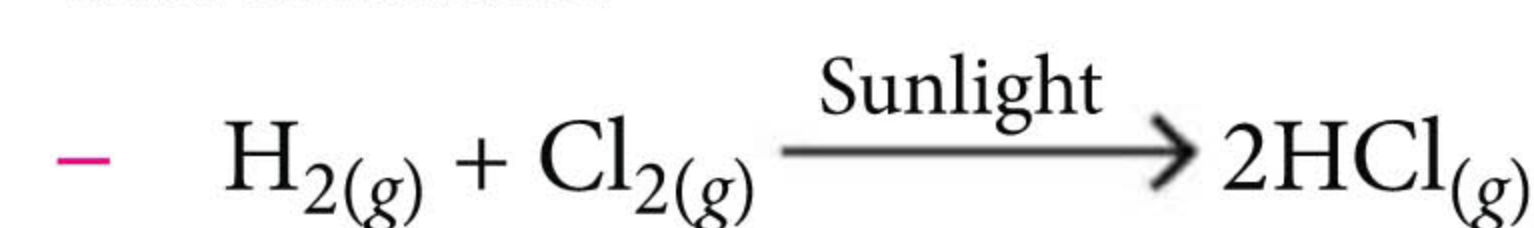


- Bleaching action of chlorine :

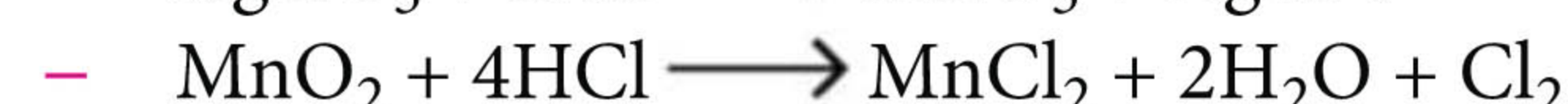
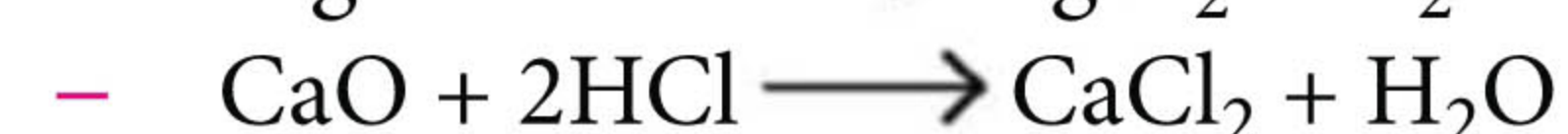


Hydrochloric Acid (HCl)

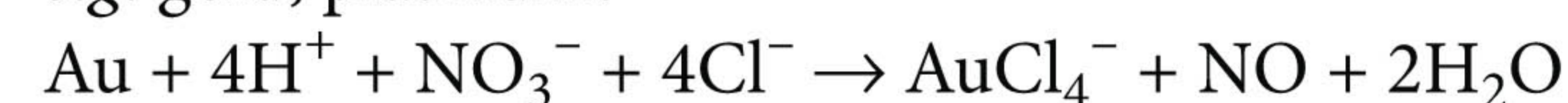
- Preparation :** By direct combination of hydrogen and chlorine.



- Properties :** Anhydrous HCl does not show acidic properties. Only aqueous HCl or in presence of moisture, HCl behaves as an acid.



When three parts of concentrated HCl and one part of concentrated HNO_3 are mixed, aqua regia is formed which is used for dissolving noble metals, e.g. gold, platinum.



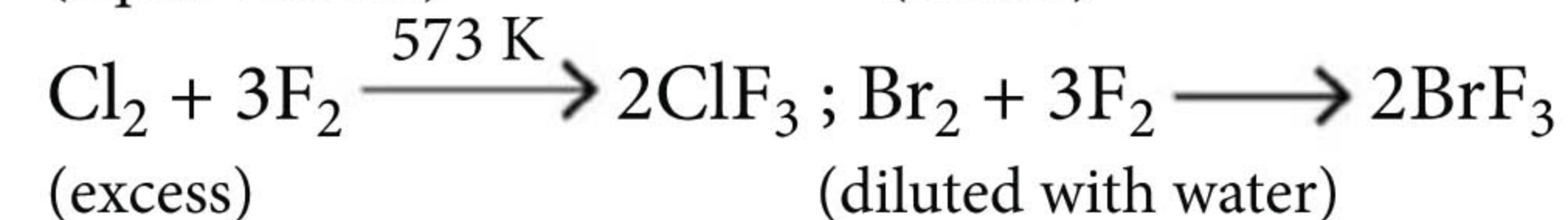
Interhalogen Compounds

- These compounds are regarded as halides of more electropositive (*i.e.* less electronegative) halogens.

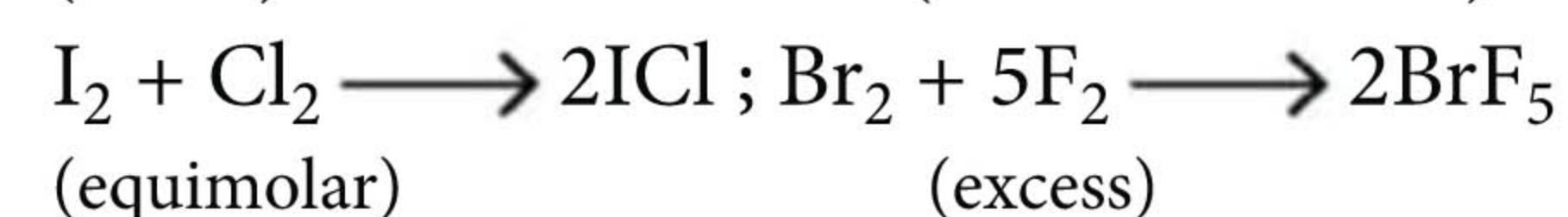
- Preparation :**



(equal volume) (excess)



(excess) (diluted with water)



(equimolar)

(excess)

- Structures :**

Type	Hybridisation	Shape	Structure
XX'	sp^3	Linear	
XX'_3	sp^3d	T-shaped	

XX'_5	sp^3d^2	Square pyramidal	
XX'_7	sp^3d^3	Pentagonal bipyramidal	

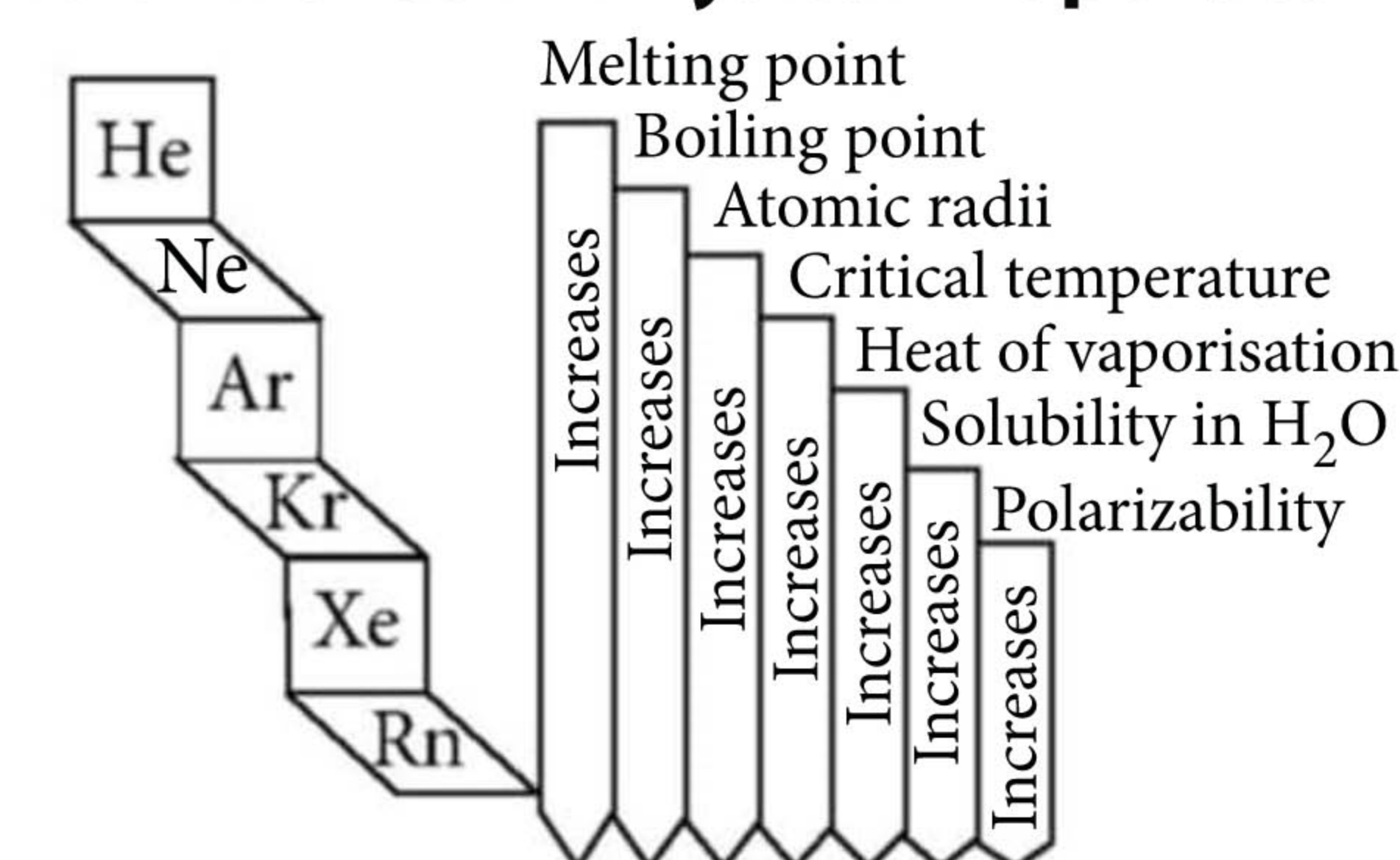
Oxyacids of Halogens

Variation of the general properties of oxyacids of halogens				
Halogen	Hypohalous acids ($X = +1$)	Halous acids ($X = +3$)	Halic acids ($X = +5$)	Perhalic acid ($X = +7$)
Cl	HClO	HClO ₂	HClO ₃	HClO ₄
Br	HBrO	—	HBrO ₃	—
I	HIO	—	HIO ₃	HIO ₄
– Oxidation number of the central atom increases (+1, +3, +5, +7) → – Thermal stability increases → – Covalent character of X—O bond increases → – Oxidising power decreases → – Basicity decreases → – Electronegativity of the central atoms remains the same —				
↓ Electronegativity of the central atom decreases — ↓ Thermal stability decreases — ↓ Oxidising power decreases — ↓ Acidic strength decreases — ↓ Oxidation number of the central atom remains the same —				

GROUP-18 ELEMENTS (NOBLE GASES)

- The elements helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe), radon (Ra) and Oganesson (Og) constitute group 18 (or zero) of the periodic table.
- All the noble gases, except He have eight electrons (closed shell) with electronic configuration $ns^2 np^6$ where $n = 2$ to 6. Helium, however has only two electrons and hence its electronic configuration is $1s^2$.

General Trends in Physical Properties



Chemical Properties

- Noble gases are generally inert and do not participate in the reactions easily. The inertness of noble gases is due to the following reasons :
 - The atoms of noble gases have stable closed shell electronic configuration.
 - Noble gases have exceptionally high ionization energies.
 - Noble gases have very low electron affinities.
- But later on few compounds of noble gases were discovered. e.g., $\text{Xe} + \text{PtF}_6 \longrightarrow \text{Xe}^+[\text{PtF}_6]^-$

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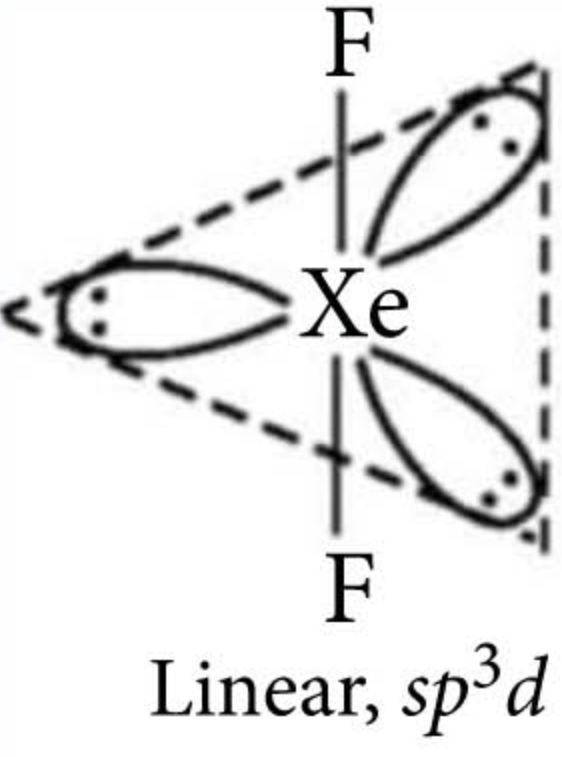
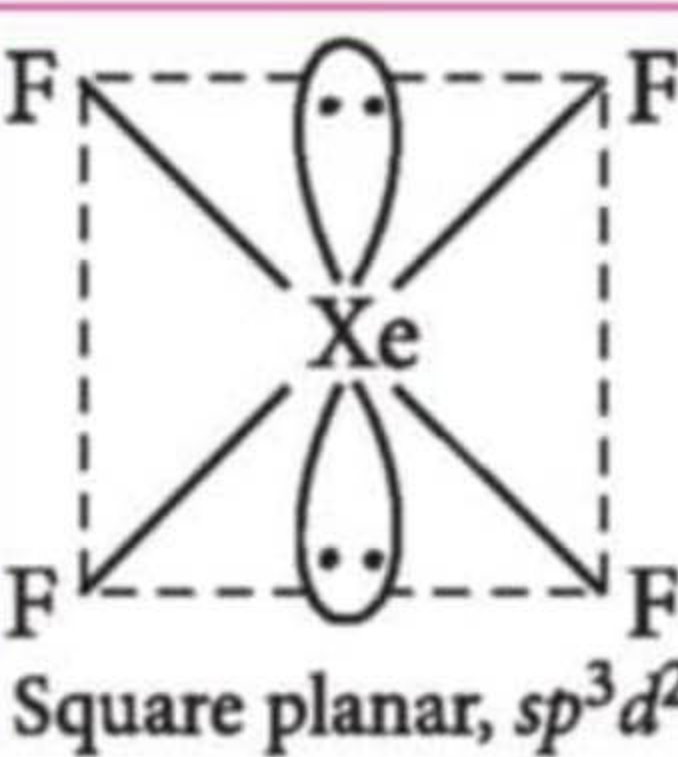
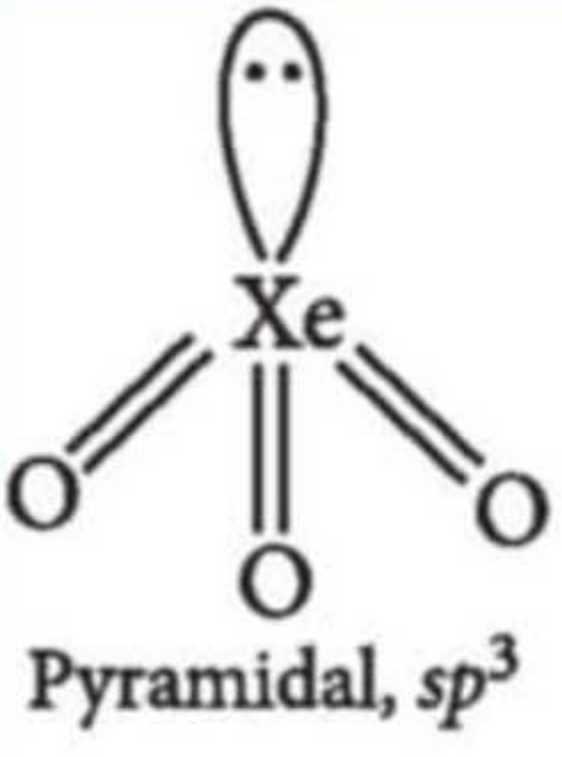
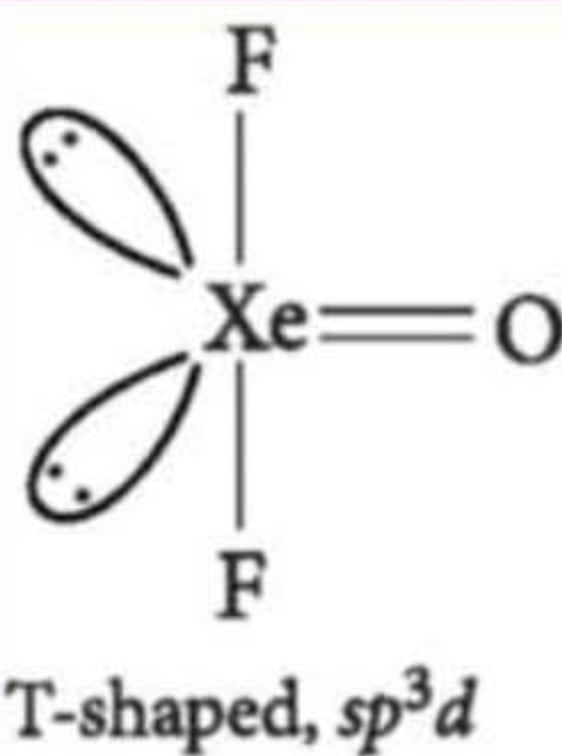
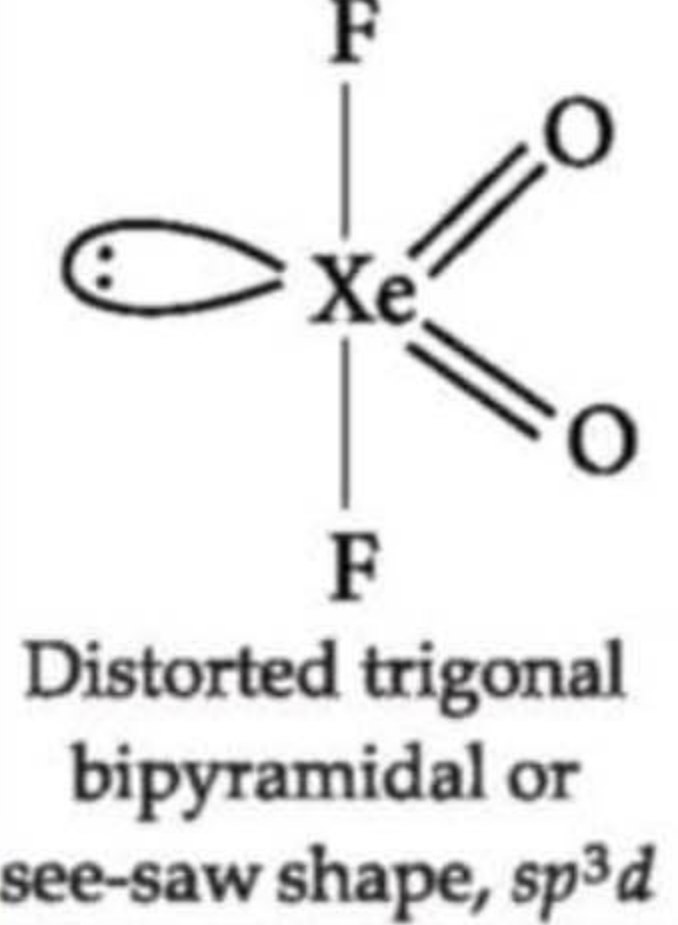
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Compounds of Xenon

Compound	Structure	Preparation	Properties
XeF ₂ , (Xenon difluoride)	 Linear, sp ³ d	$\text{Xe} + \text{F}_2 \xrightarrow[400^\circ\text{C}]{\text{Ni tube}} \text{XeF}_2$ (2 : 1) $\text{Xe} + \text{O}_2\text{F}_2 \xrightarrow{118^\circ\text{C}} \text{XeF}_2 + \text{O}_2$	$\text{XeF}_2 \xrightarrow{\text{H}_2} \text{Xe} + 2\text{HF}$ $\text{XeF}_2 \xrightarrow{\text{H}_2\text{O}} \text{Xe} + 2\text{HF} + \frac{1}{2}\text{O}_2$ $\text{XeF}_2 \xrightarrow{2\text{NO}} \text{Xe} + 2\text{NOF}$ $\text{XeF}_2 \xrightarrow{2\text{HCl}} \text{Xe} + 2\text{HF} + \text{Cl}_2$ – Acts as a fluorinating agent.
XeF ₄ , (Xenon tetrafluoride)	 Square planar, sp ³ d ²	$\text{Xe} + 2\text{F}_2 \xrightarrow[600^\circ\text{C}]{\text{Ni tube}} \text{XeF}_4$ (1 : 5)	– Colourless, crystalline solid with melting point, 117.1°C. – $\text{XeF}_4 + 2\text{H}_2 \rightarrow \text{Xe} + 4\text{HF}$ – Undergoes disproportionation in water. $6\text{XeF}_4 + 12\text{H}_2\text{O} \rightarrow 4\text{Xe} + 2\text{XeO}_3 + 24\text{HF} + 3\text{O}_2$ – Gives adduct. $\text{XeF}_4 + \text{SbF}_5 \rightarrow [\text{XeF}_3]^+ [\text{SbF}_6]^-$ – Acts as a fluorinating agent. – Dissolves in anhydrous HF.
XeO ₃ , (Xenon trioxide)	 Pyramidal, sp ³	Complete hydrolysis of XeF ₄ and XeF ₆ : $6\text{XeF}_4 + 12\text{H}_2\text{O} \rightarrow 4\text{Xe} + 2\text{XeO}_3 + 3\text{O}_2 + 24\text{HF}$ $\text{XeF}_6 + 3\text{H}_2\text{O} \rightarrow \text{XeO}_3 + 6\text{HF}$	– Colourless, highly explosive and powerful oxidising agent. – With water forms xenic acid. $\text{XeO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{XeO}_4$ – Undergoes disproportionation when dissolved in alkali. $2\text{XeO}_3 + 4\text{OH}^- \rightarrow \text{Xe} + \text{O}_2 + \text{XeO}_6^{4-} + 2\text{H}_2\text{O}$
XeOF ₂ , (Xenon oxydifluoride)	 T-shaped, sp ³ d	Partial hydrolysis of XeF ₄ : $\text{XeF}_4 + \text{H}_2\text{O} \rightarrow \text{XeOF}_2 + 2\text{HF}$	Unstable
XeO ₂ F ₂ , (Xenon dioxydifluoride)	 Distorted trigonal bipyramidal or see-saw shape, sp ³ d	Partial hydrolysis of XeOF ₄ or XeF ₆ : $\text{XeOF}_4 + \text{H}_2\text{O} \rightarrow \text{XeO}_2\text{F}_2 + 2\text{HF}$ $\text{XeF}_6 + 2\text{H}_2\text{O} \rightarrow \text{XeO}_2\text{F}_2 + 4\text{HF}$ Action of SiO ₂ on XeOF ₄ : $2\text{XeOF}_4 + \text{SiO}_2 \rightarrow 2\text{XeO}_2\text{F}_2 + \text{SiF}_4$	Colourless solid. Undergoes hydrolysis readily. $\text{XeO}_2\text{F}_2 + \text{H}_2\text{O} \rightarrow \text{XeO}_3 + 2\text{HF}$

PEEP INTO PREVIOUS YEARS

9. The type of hybridisation and number of lone pair(s) of electrons of Xe in XeOF₄, respectively, are
(a) sp³d and 2 (b) sp³d² and 2
(c) sp³d² and 1 (d) sp³d and 1
(JEE Main 2019)

10. The correct statement(s) about the oxoacids, HClO₄ and HClO, is(are)
(a) the conjugate base of HClO₄ is weaker base than H₂O
(b) the central atom in both HClO₄ and HClO is sp³ hybridized

- (c) HClO₄ is formed in the reaction between Cl₂ and H₂O
(d) HClO₄ is more acidic than HClO because of the resonance stabilization of its anion.
(JEE Advanced 2017)

11. Which one of the following orders is correct for the bond dissociation enthalpy of halogen molecules?
(a) Br₂ > I₂ > F₂ > Cl₂ (b) F₂ > Cl₂ > Br₂ > I₂
(c) I₂ > Br₂ > Cl₂ > F₂ (d) Cl₂ > Br₂ > F₂ > I₂
(NEET-I 2016)

POINTS FOR EXTRA SCORING

- XeF₆ forms adducts with BF₃, GeF₄, SnF₄ along with SbF₅, AsF₅ and PF₅.
- Acidic strength order : N₂O₅ > P₂O₅ > As₂O₅ > Sb₂O₅ > Bi₂O₅
- The acidic nature order : SO₂ > SeO₂ > TeO₂ > PoO₂ and SO₃ > SeO₃ > TeO₃
- Strength of the conjugate bases : ClO⁻ > ClO₂⁻ > ClO₃⁻ > ClO₄⁻

- Anions stability of oxoacids : ClO⁻ < ClO₂⁻ < ClO₃⁻ > ClO₄⁻
- Order of oxidising power is : Cl₂O > ClO₂ > Cl₂O₆ > Cl₂O₇
- Order of stability Cl₂O < ClO₂ < Cl₂O₆ < Cl₂O₇
- Strength of M – X bond (covalent) : M – F > M – Cl > M – Br > M – I
- Ionic character of M – X bond, melting point and boiling point : M – F > M – Cl > M – Br > M – I
- Heat of hydration and basic character : F⁻ > Cl⁻ > Br⁻ > I⁻ reducing character increases in the order : F⁻ < Cl⁻ < Br⁻ < I⁻
- Noble gases neither act as reducing agents nor as oxidising agents.
- Charcoal dissolves slowly in hot dilute HNO₃ forming a brown coloured substance known as artificial tannin.
- Sulphur is also called as ‘brimstone’.
- H₂S is called sulphuretted hydrogen.

Answer Key For Peep Into Previous Years

1. (b,c,d) 2. (a) 3. (b) 4. (d) 5. (c) 6. (d)
7. (a) 8. (c) 9. (c) 10. (a,b,d) 11. (d)



1. In the cyanide extraction process of silver from argentite ore, the oxidising and reducing agent used are
(a) O₂ and CO respectively
(b) O₂ and Zn dust respectively
(c) HNO₃ and Zn dust respectively
(d) HNO₃ and CO respectively.
2. The maximum number of P – H bonds are contained in which of the following molecules?
(a) H₃PO₂ (b) H₃PO₃
(c) H₃PO₄ (d) H₄P₂O₇
3. The extraction principle used in extraction of a metal ‘M’ can be represented as follows :
 $MS + 2\text{O}_2 \rightarrow \text{MSO}_4$
 $\text{MSO}_4 + MS \rightarrow 2M + 2\text{SO}_2$

The metal ‘M’ is

- (a) Mg (b) Pb
(c) Sn (d) Fe

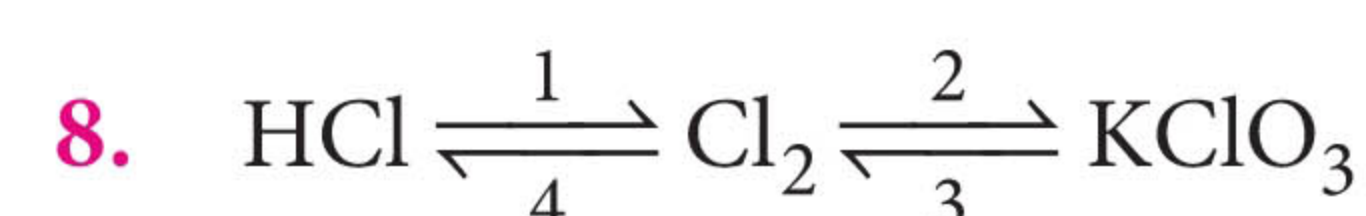
4. The incorrect statement(s) about O₃ is
(a) O – O bond lengths are equal
(b) O₃ is diamagnetic in nature
(c) thermal decomposition of O₃ is endothermic
(d) O₃ has a bent structure.
5. $\text{AlCl}_3 + \text{BCl}_3 \xrightarrow{\text{Excess}} \text{AlCl}_4 + \text{B} \downarrow$
 $\text{BO} \xrightarrow{\text{Heat}} \text{B} + 1/2\text{O}_2$
(A and B are metals)
The ore of B is
(a) cinnabar (b) azurite
(c) galena (d) siderite.

6. A hydride (X) of a group-15 element is distinctly basic and has unexpectedly high boiling point. It reacts with NaOCl to give another hydride (Y) which is a strong reducing agent and is used in organic analysis. X and Y are

(a) PH_3 , P_2H_4 (b) NH_3 , N_2H_4
(c) AsH_3 , As_2H_4 (d) NH_3 , NH_2Cl

7. Which of the following statements is correct according to the basic concepts of thermodynamics which govern the feasibility of a metallurgical process?

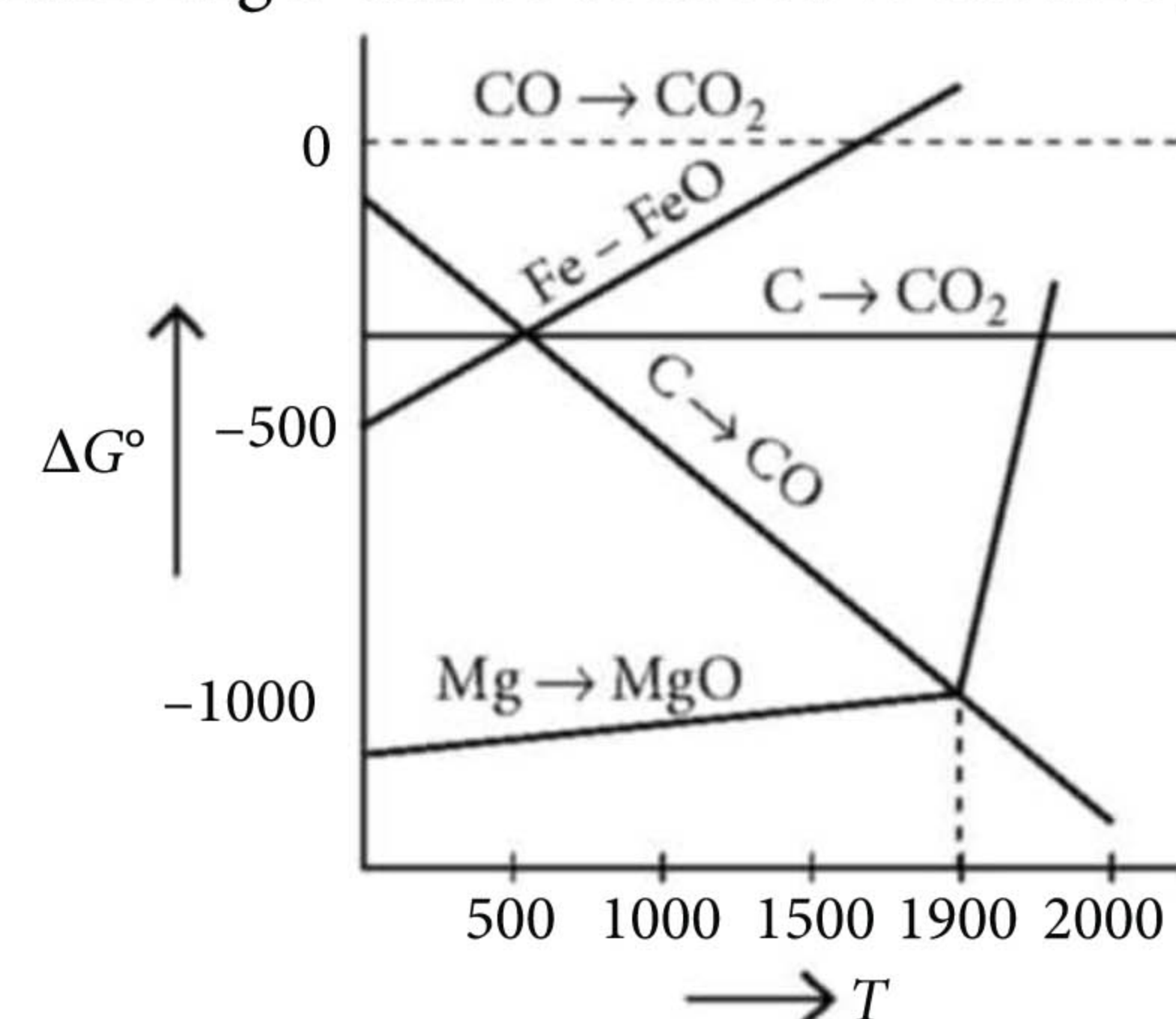
(a) When the value of ΔG is positive for the equation $\Delta G = \Delta H - T\Delta S$, the reaction will proceed.
(b) If reactants and products of two reactions are put together and net ΔG is -ve, the overall reaction will occur.
(c) On increasing the temperature, the value of ΔG becomes +ve.
(d) Feasibility of thermal oxidation of an ore can be established by Ellingham diagram in which a straight line shows that the reduction reaction will proceed.



In the above sequence of reactions, the steps 2 and 3 require following reagents respectively?

(a) NaOH, I_2 (b) HCl, I_2
(c) KOH, I_2 (d) KOH, O_2

9. Using the Ellingham diagram predict the temperature at which MgO can be reduced to metal by carbon.



(a) Below 1500 °C (b) Below 1120 °C
(c) Above 1900 °C (d) Below 1600 °C

10. In alkaline solution HXeO_4^- disproportionates to
(a) XeO_6^{4-} and Xe (b) XeO_4^{2-} and XeO_3
(c) XeO_3 and Xe (d) XeO_6^{4-} and XeO_3

11. Native silver metal forms a water soluble complex with a dilute aqueous solution of NaCN in the presence of

(a) nitrogen (b) oxygen
(c) carbon dioxide (d) argon.

12. The products of the chemical reaction between $\text{Na}_2\text{S}_2\text{O}_3$, Cl_2 and H_2O are

(a) $\text{S} + \text{HCl} + \text{Na}_2\text{S}$ (b) $\text{S} + \text{HCl} + \text{Na}_2\text{SO}_4$
(c) $\text{S} + \text{HCl} + \text{Na}_2\text{S}_2\text{O}_3$ (d) $\text{S} + \text{NaClO}_3 + \text{H}_2\text{O}$

13. Which of the following statements are incorrect?

I. Zinc can be extracted by self-reduction.
II. A depressant prevents certain type of particles to come to the froth.
III. Copper matte contains ZnS and Cu_2S .
IV. The solidified copper obtained from reverberatory furnace has blistered appearance due to evolution of SO_2 during the extraction.
(a) I and II (b) II and III
(c) I and III (d) II and IV

14. Sulphur reacts with chlorine in 1 : 2 ratio and forms (X). (X) on hydrolysis gives a sulphur compound (Y). What is the hybridized state of central atom in the anion of (Y)?

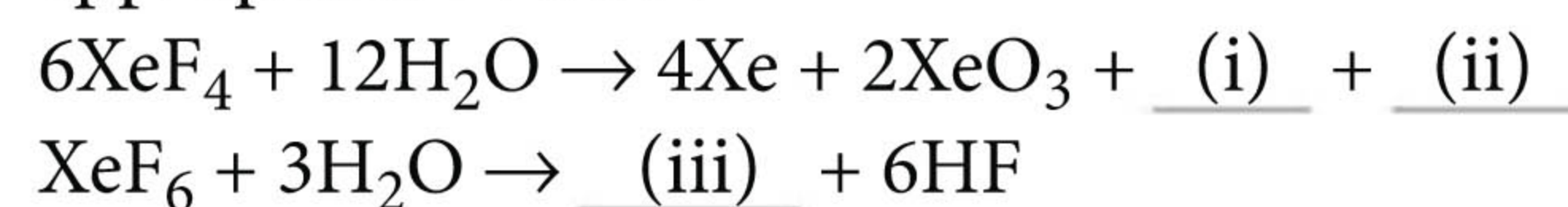
(a) sp (b) sp^3 (c) sp^2 (d) sp^3d

15. Which of the following are main requirements for vapour phase refining?

(i) Metal should form a volatile compound with the reagent.
(ii) The volatile compound should be easily decomposable to give back pure metal.
(iii) Metal should be very reactive and form a stable compound with the reagent.

(a) (i), (ii) and (iii) (b) Only (i) and (ii)
(c) Only (ii) and (iii) (d) Only (i) and (iii)

16. Complete the following reactions by filling the appropriate choice :



(i) (ii) (iii)
(a) F_2 H_2O XeOF_4
(b) 24HF 3O_2 XeO_3
(c) 12HF $2\text{H}_2\text{O}$ XeO
(d) HF H_2O Xe_2O_3

17. From the Ellingham graphs on carbon, which of the following statements is false ?

(a) CO_2 is more stable than CO at less than 983 K.
(b) CO reduces Fe_2O_3 to Fe at less than 983 K.

(c) CO is less stable than CO_2 at more than 983 K.
(d) CO reduces Fe_2O_3 to Fe in the reduction zone of blast furnace.

18. The oxidation number of chlorine in the final product B in the following sequence of reaction is
 $\text{KClO}_4 + \text{conc. H}_2\text{SO}_4 \longrightarrow \text{KHSO}_4 + \text{A}$
 $\text{A} + \text{P}_2\text{O}_5 \longrightarrow \text{B}$

(a) +3 (b) +5 (c) +7 (d) -1

19. Sulphide ores are common for metals

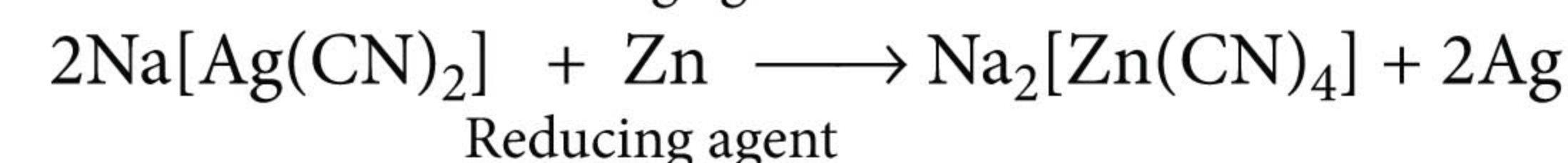
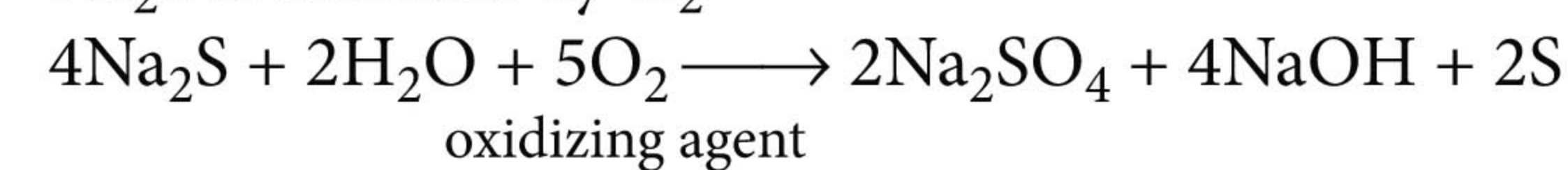
(a) Ag, Cu and Pb (b) Ag, Cu and Sn
(c) Ag, Mg and Pb (d) Al, Cu and Pb

20. In which of the following reactions O_2 is not formed as one of the product?

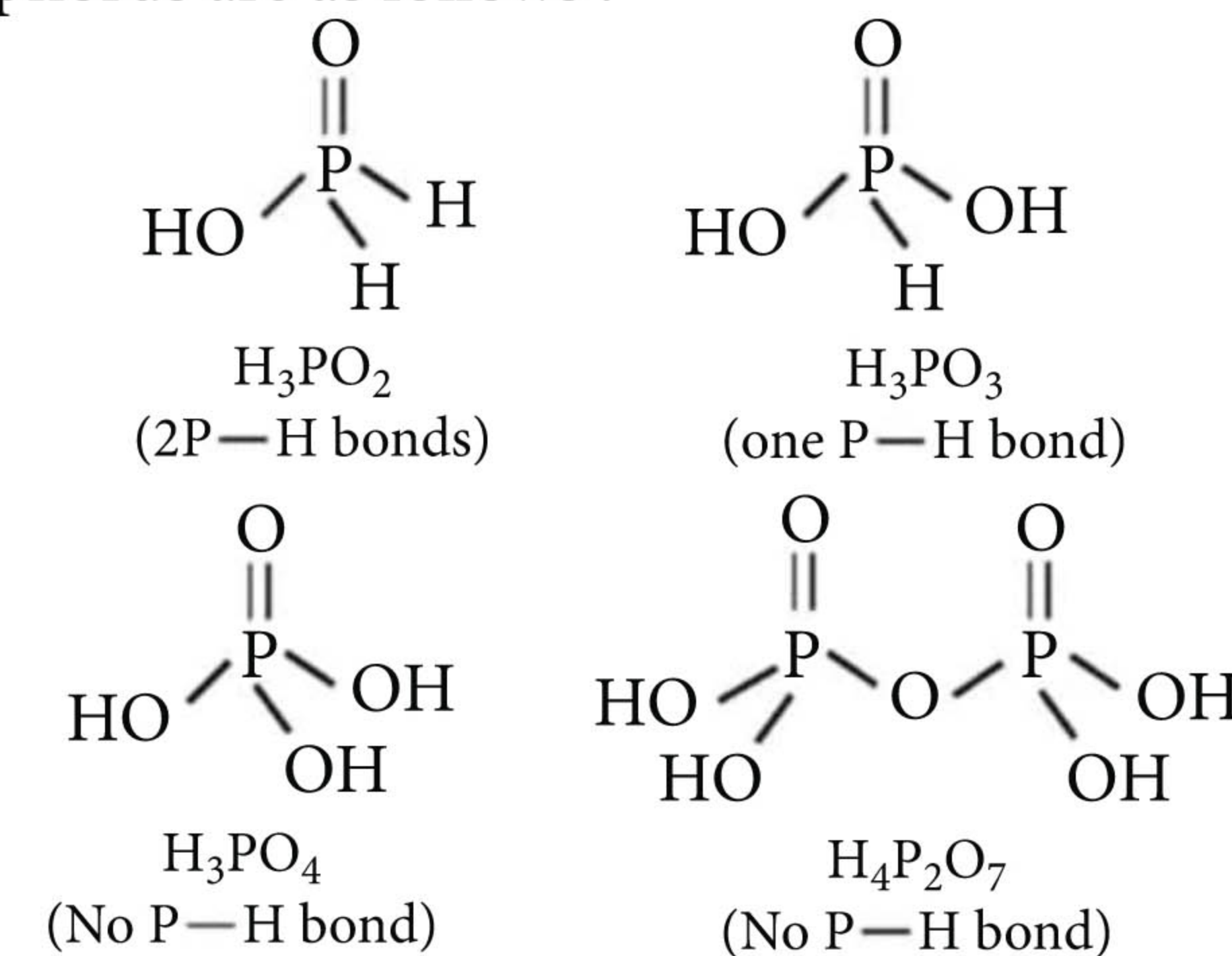
(a) $\text{KClO}_3 \xrightarrow[\text{Heat}]{\text{MnO}_2}$
(b) $\text{SnCl}_2 + \text{HCl} + \text{O}_3 \longrightarrow$
(c) $\text{FeSO}_4 + \text{H}_2\text{SO}_4 + \text{O}_3 \longrightarrow$
(d) $\text{PbS} + \text{O}_3 \longrightarrow$

SOLUTIONS

1. (b): $\text{Ag}_2\text{S} + 4\text{NaCN} \longrightarrow 2\text{Na}[\text{Ag}(\text{CN})_2] + \text{Na}_2\text{S}$
 Na_2S is oxidised by O_2



2. (a): The structures of the given oxyacids of phosphorus are as follows :

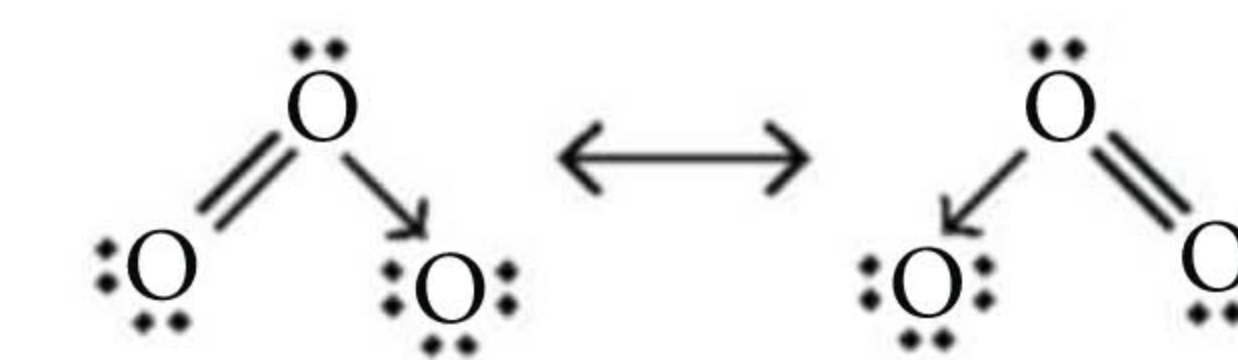


Thus, H_3PO_2 contains the maximum number of P—H bonds.

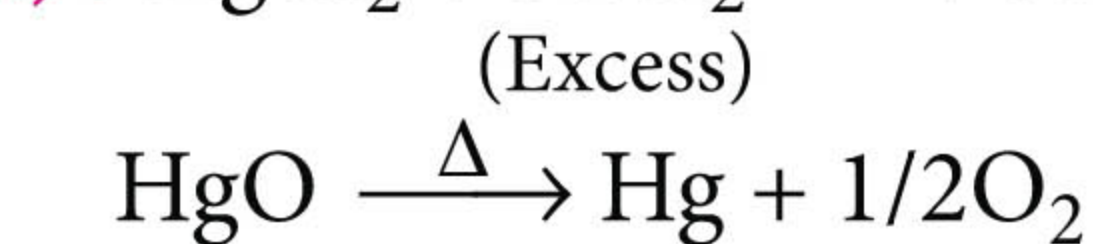
3. (b): Reactions show auto reduction.

Auto reduction method is used in the metallurgy of Pb, Hg and Cu etc.

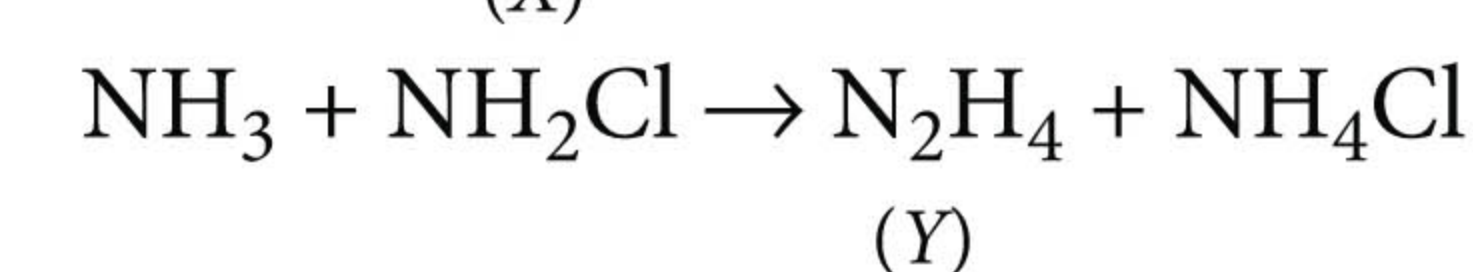
4. (c): On account of resonance, bond lengths are same (1.28 Å). In this molecule, all electrons paired, so it is diamagnetic. It has bent structure. Its formation is endothermic and hence, decomposition is exothermic.



5. (a): $\text{HgCl}_2 + \text{SnCl}_2 \longrightarrow \text{SnCl}_4 + \text{Hg}$



6. (b): $\text{NH}_3 + \text{NaOCl} \xrightarrow[\text{(X)}]{\text{glue}} \text{NH}_2\text{Cl} + \text{NaOH}$



7. (b)

8. (c): Cl_2 in KOH disproportionates forming KCl and KClO_3 . As I_2 is more electropositive than Cl_2 , I_2 displaces Cl_2 from KClO_3 .

9. (c): Above 1900°C, the Mg—MgO line goes above the line C—CO. So, the reaction is feasible above 1900°C.

10. (a): $2\text{HXeO}_4^- + 2\text{OH}^- \xrightarrow[\text{perxenate ion}]{+6 \quad +8 \quad 0} \text{XeO}_6^{4-} + \text{Xe} + 2\text{H}_2\text{O} + \text{O}_2$

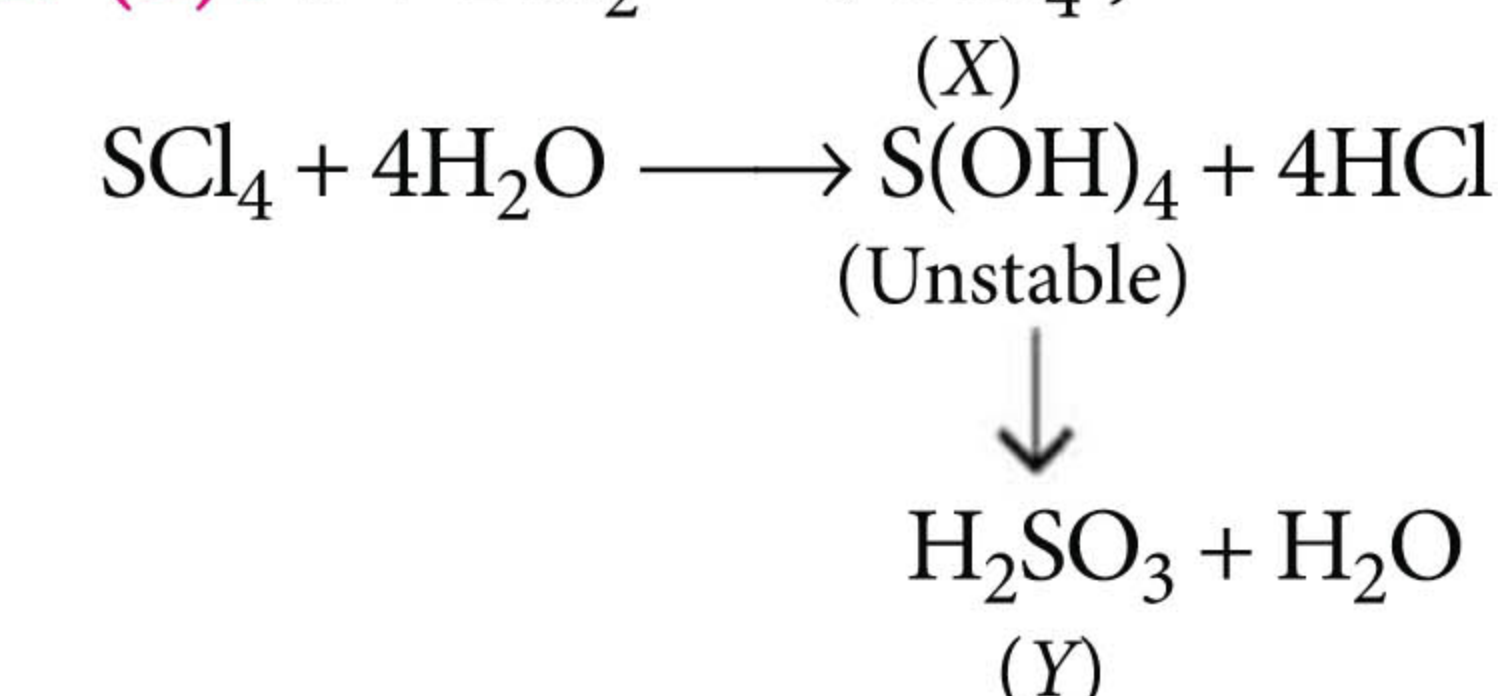
Thus, HXeO_4^- disproportionates to XeO_6^{4-} (by oxidation) and Xe (by reduction).

11. (b): $4\text{Ag} + 8\text{NaCN} + 2\text{H}_2\text{O} + \text{O}_2 \longrightarrow 4\text{Na}[\text{Ag}(\text{CN})_2] + \text{NaOH}$
Sodium argentocyanide
(water soluble)

12. (b): $\text{Na}_2\text{S}_2\text{O}_3 + \text{Cl}_2 + \text{H}_2\text{O} \longrightarrow \text{S} + 2\text{HCl} + \text{Na}_2\text{SO}_4$

13. (c): Zinc cannot be extracted by self-reduction and copper matte consists of Cu_2S and FeS.

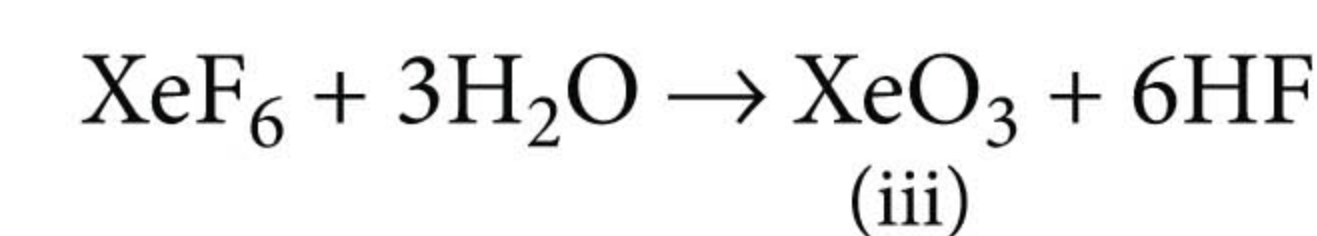
14. (b): $\text{S} + 2\text{Cl}_2 \longrightarrow \text{SCl}_4$;



The hybridized state of S in SO_3^{2-} is sp^3 .

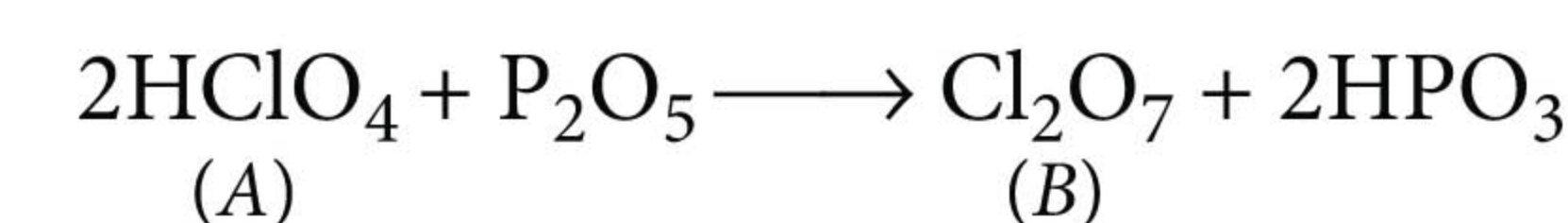
15. (b)

16. (b): $6\text{XeF}_4 + 12\text{H}_2\text{O} \longrightarrow 4\text{Xe} + 2\text{XeO}_3 + 24\text{HF} + 3\text{O}_2$
(i) (ii)



17. (c)

18. (c): $\text{KClO}_4 + \text{conc. H}_2\text{SO}_4 \longrightarrow \text{KHSO}_4 + \text{HClO}_4$
(A)



19. (a)

20. (b): $3\text{SnCl}_2 + 6\text{HCl} + \text{O}_3 \longrightarrow 3\text{SnCl}_4 + 3\text{H}_2\text{O}$



CBSE

warm-up!

CLASS-XII

Chapterwise practice questions for CBSE Exams as per the latest pattern and marking scheme issued by CBSE for the academic session 2019-20.

Series 4 The d- and f-Block Elements | Coordination Compounds

Time Allowed : 3 hours
Maximum Marks : 70

GENERAL INSTRUCTIONS

- All questions are compulsory.
- Section A : Q. no. 1 to 20 are very short answer-objective questions and carry 1 mark each.
- Section B : Q. no. 21 to 27 are short answer questions and carry 2 marks each.
- Section C : Q. no. 28 to 34 are long answer-I questions and carry 3 marks each.
- Section D : Q. no. 35 to 37 are long answer-II questions and carry 5 marks each.
- There is no overall choice in the question paper. However, internal choices are given in the sections.
- Use log tables if necessary, use of calculator is not allowed.

SECTION - A

- Amongst TiF_6^{2-} , CoF_6^{3-} , Cu_2Cl_2 and NiCl_4^{2-} (at. nos. Ti = 22, Co = 27, Cu = 29, Ni = 28), the colourless species are
(a) CoF_6^{3-} and NiCl_4^{2-} (b) TiF_6^{2-} and CoF_6^{3-}
(c) Cu_2Cl_2 and NiCl_4^{2-} (d) TiF_6^{2-} and Cu_2Cl_2
- The formula of sodium nitroprusside is
(a) $\text{Na}_4[\text{Fe}(\text{CN})_5\text{NOS}]$ (b) $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$
(c) $\text{NaFe}[\text{Fe}(\text{CN})_6]$ (d) $\text{Na}_2[\text{Fe}(\text{CN})_6\text{NO}_2]$
- Which of the following is most basic?
(a) $\text{Ce}(\text{OH})_3$ (b) $\text{Lu}(\text{OH})_3$
(c) $\text{Yb}(\text{OH})_3$ (d) $\text{Tb}(\text{OH})_3$
- Which of the following pairs represents linkage isomers?
(a) $[\text{Cu}(\text{NH}_3)_4][\text{PtCl}_4]$ and $[\text{Pt}(\text{NH}_3)_4][\text{CuCl}_4]$
(b) $[\text{Pd}(\text{PPh}_3)_2(\text{NCS})_2]$ and $[\text{Pd}(\text{PPh}_3)_2(\text{SCN})_2]$
(c) $[\text{Co}(\text{NH}_3)_5(\text{NO}_3)]\text{SO}_4$ and $[\text{Co}(\text{NH}_3)_5(\text{SO}_4)]\text{NO}_3$
(d) $[\text{PtCl}_2(\text{NH}_3)_4]\text{Br}_2$ and $[\text{PtBr}_2(\text{NH}_3)_4]\text{Cl}_2$

- Number of electrons transferred in each case when KMnO_4 acts as an oxidising agent to give MnO_2 , Mn^{2+} , $\text{Mn}(\text{OH})_3$ and MnO_4^{2-} , are respectively
(a) 3, 5, 4 and 1 (b) 4, 3, 1 and 5
(c) 1, 3, 4 and 5 (d) 5, 4, 3 and 1
- Amongst $[\text{Ni}(\text{CO})_4]$, $[\text{Ni}(\text{CN})_4]^{2-}$ and $[\text{NiCl}_4]^{2-}$
(a) $[\text{Ni}(\text{CO})_4]$ and $[\text{NiCl}_4]^{2-}$ are diamagnetic and $[\text{Ni}(\text{CN})_4]^{2-}$ is paramagnetic
(b) $[\text{NiCl}_4]^{2-}$ and $[\text{Ni}(\text{CN})_4]^{2-}$ are diamagnetic and $[\text{Ni}(\text{CO})_4]$ is paramagnetic
(c) $[\text{Ni}(\text{CO})_4]$ and $[\text{Ni}(\text{CN})_4]^{2-}$ are diamagnetic and $[\text{NiCl}_4]^{2-}$ is paramagnetic
(d) $[\text{Ni}(\text{CO})_4]$ is diamagnetic and $[\text{NiCl}_4]^{2-}$ and $[\text{Ni}(\text{CN})_4]^{2-}$ are paramagnetic.
- Cerium ($Z = 58$) is an important member of the lanthanoids. Which of the following statements about it is incorrect?
(a) Ce(IV) acts as an oxidant.
(b) The +3 oxidation state of Ce is more stable than +4 oxidation.

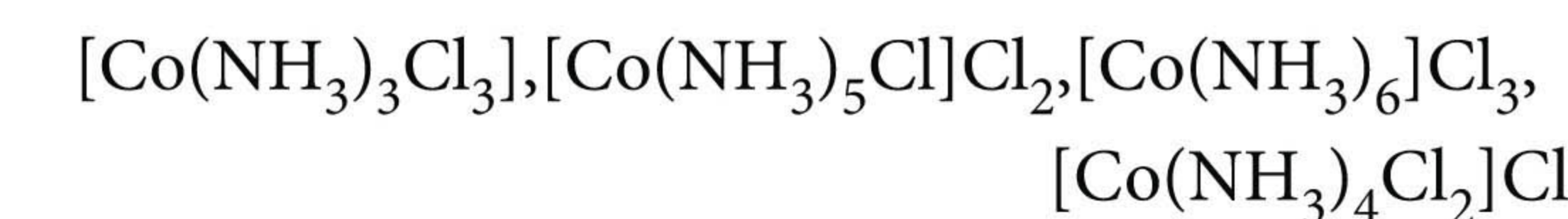
- The +4 oxidation state of Ce is not known in solution state.
- The common oxidation states of Ce are +3 and +4.

- Among the following metal carbonyls, the C — O bond order is the lowest in
(a) $[\text{Mn}(\text{CO})_6]^+$ (b) $[\text{Fe}(\text{CO})_5]$
(c) $[\text{Cr}(\text{CO})_6]$ (d) $[\text{V}(\text{CO})_6]^-$
- The magnetic moment of a transition metal ion is found to be 3.87 B.M. The number of unpaired electrons present in it is
(a) 2 (b) 3 (c) 4 (d) 5
- Which of the following statements is incorrect?
(a) In $\text{K}_3[\text{Fe}(\text{CN})_6]$, the ligand has satisfied only the secondary valency of ferric ion.
(b) In $\text{K}_3[\text{Fe}(\text{CN})_6]$, the ligand has satisfied both primary and secondary valencies of ferric ion.
(c) In $\text{K}_4[\text{Fe}(\text{CN})_6]$, the ligand has satisfied both primary and secondary valencies of ferrous ion.
(d) In $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$, the ligand has satisfied only the secondary valency of copper.

- Why does Ti^{4+} ion show diamagnetic behaviour?
- Write the names of the following complexes using IUPAC norms :
(i) $\text{Na}_3[\text{AlF}_6]$ (ii) $[\text{CoCl}(\text{en})_2(\text{ONO})]\text{Cl}$
- Which metal in the first series of transition element shows the highest number of oxidation states?
- What is crystal field splitting?
- Which compound is generally used in making optical glasses such as Crooke's lenses which protect eyes against UV light?
- Explain the difference between a weak field ligand and a strong field ligand.
- Explain why Zn shows only +2 oxidation state.
- How many ions are produced from the complex, $\text{Co}(\text{NH}_3)_6\text{Cl}_2$ in solution?
- Give reason for the following :
Actinoids exhibit a greater range of oxidation states than lanthanoids.
(AI 2014 C, AI 2012, Delhi 2011)
- Which isomer, *cis*- or *trans*- of the complex $[\text{Co}(\text{en})_2\text{Cl}_2]^+$, does not show optical isomerism?

SECTION - B

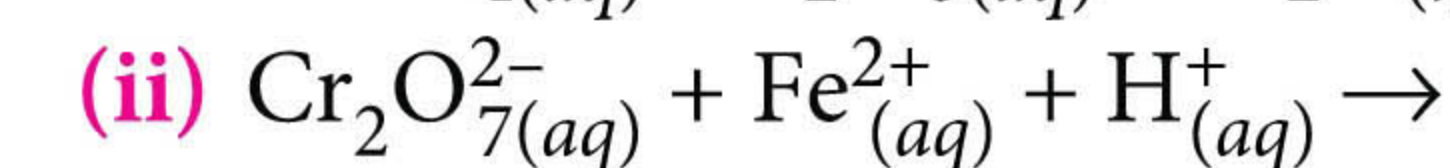
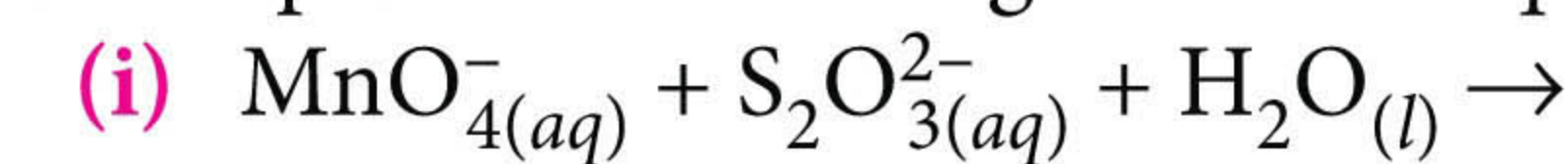
- Copper (I) is diamagnetic, whereas copper (II) is paramagnetic. Give reason.
- Arrange the following complexes in order of increasing electrical conductivity:



OR

What is the difference between $[\text{Co}(\text{CN})_6]^{3-}$ and $[\text{CoF}_6]^{3-}$ however both are octahedral complexes?

- Complete the following chemical equations :



(AI 2011, 2010)

- Why is copper sulphate pentahydrate coloured?
- What happens when
(i) potassium dichromate reacts with sulphur dioxide in acidic medium?
(ii) potassium dichromate reacts with Mohr's salt in presence of dil. H_2SO_4 ?

OR

Draw the structures of chromate and dichromate ions.

- How is the magnetic moment of a species related to the number of unpaired electrons? Explain giving examples.
- What is the effect of pH on the colour of the solution of potassium dichromate?

SECTION - C

- Write the hybridisation and magnetic character of the following complexes:
(i) $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ (ii) $[\text{Ni}(\text{CN})_4]^{2-}$
[Atomic number : Fe = 26, Ni = 28] (AI 2019)
- Account for the following :
(i) Oxidizing power in the series : $\text{VO}^{2+} < \text{Cr}_2\text{O}_7^{2-} < \text{MnO}_4^-$
(ii) Actinoid contraction is greater from element to element than lanthanoid contraction.
(iii) Oxoanions of a metal show higher oxidation states.

OR

- A blackish brown coloured solid 'A' when fused with alkali metal hydroxides in presence of air, produces a dark green coloured compound 'B', which on electrolytic oxidation in alkaline medium gives a dark purple coloured compound C. Identify A, B and C and write the reactions involved
- What happens when an acidic solution of the green compound (B) is allowed to stand for sometime? Give the equation involved. What is this type of reaction called?

30. (i) What is the coordination number of central metal ion in $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$?
 (ii) Mention the factors on which stability of the complexes depends.

OR

Define *cis* and *trans* isomerism in complexes giving suitable examples.

31. Assign reason for each of the following :

- (i) Mn shows the highest oxidation state of +7 with oxygen but with fluorine it shows the highest oxidation state of +4.
 (ii) E° for $\text{Mn}^{3+}/\text{Mn}^{2+}$ couple is more positive than for $\text{Fe}^{3+}/\text{Fe}^{2+}$.
 (iii) The transition elements form interstitial compounds.
32. Deduce the structures of $[\text{NiCl}_4]^{2-}$ and $[\text{Ni}(\text{CO})_4]$ considering the hybridisation of the metal ion. Calculate the magnetic moment (spin only) of the species.

33. Predict which of the following will be coloured in aqueous solution?

Ti^{3+} , V^{3+} , Cu^+ , Sc^{3+} , Mn^{2+} and Fe^{3+}

Give reason for each.

34. Draw figures to show splitting of degenerate *d*-orbitals in an octahedral and in a tetrahedral crystal field.

SECTION - D

35. Explain the following properties of transition elements :

- (a) metallic character (b) ionisation energies
 (c) variable oxidation states.

OR

- (i) Compare the chemistry of actinoids with that of the lanthanoids with special reference to :

- (a) electronic configuration.
 (b) oxidation state.
 (c) atomic and ionic sizes

- (ii) How would you account for the following:

- (a) Of the d^4 species, Cr^{2+} is strongly reducing while manganese (III) is strongly oxidising.
 (b) Cobalt (II) is stable in aqueous solution but in the presence of complexing reagents it is easily oxidised.

36. Write down the IUPAC name for each of the following complexes and indicate the oxidation state, electronic configuration and coordination number. Also give geometry and magnetic moment of the complexes :

- (a) $\text{K}[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$
 (b) $[\text{CrCl}_3(\text{py})_3]$ (c) $\text{K}_4[\text{Mn}(\text{CN})_6]$
 (d) $\text{Co}[(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ (e) $\text{Cs}[\text{FeCl}_4]$

OR

- (i) Write the main assumptions of valence bond theory.
 (ii) What do you mean by inner orbital complexes and outer orbital complexes? Give examples of each.

37. (i) Explain giving reason which one of the following pair has the property indicated :

- (a) Fe or Cu has higher melting point.
 (b) Co^{2+} or Ni^{2+} has lower magnetic moment.

(Atomic numbers : Fe = 26, Co = 27, Ni = 28, Cu = 29)

- (ii) Write chemical equations for the conversion of
 (a) chromite ore to sodium chromate
 (b) pyrolusite to potassium manganate
 (c) potassium permanganate to manganese dioxide.

OR

What is lanthanide contraction ? Discuss its cause and consequences.

SOLUTIONS

1. (d) : Oxidation state of

Ti in $\text{TiF}_6^{2-} = +4$ i.e., $\text{Ti}^{4+} \longrightarrow 3d^0$

Co in $\text{CoF}_6^{3-} = +3$ i.e., $\text{Co}^{3+} \longrightarrow 3d^6$

Ni in $\text{NiCl}_4^{2-} = +2$ i.e., $\text{Ni}^{2+} \longrightarrow 3d^8$

Cu in $\text{Cu}_2\text{Cl}_2 = +1$ i.e., $\text{Cu}^+ \longrightarrow 3d^{10}$

Colour of salts is due to partially filled *d*-orbitals. Since, TiF_6^{2-} has completely empty *d*-subshell and Cu_2Cl_2 involves completely filled *d*-subshell, so these are colourless salts.

2. (b)

3. (a) : $\text{Ce}(\text{OH})_3$ is strongest base. As the size of the lanthanide ions decreases from Ce^{3+} to Lu^{3+} , the covalent character of *M* – OH bond increases and hence the basic strength decreases.

Thus, $\text{Ce}(\text{OH})_3$ is most basic while $\text{Lu}(\text{OH})_3$ is least basic.

4. (b) : Linkage isomerism is exhibited by compounds containing ambidentate ligands.

In $[\text{Pd}(\text{PPh}_3)_2(\text{NCS})_2]$, the linkage of NCS and Pd is through N.

In $[\text{Pd}(\text{PPh}_3)_2(\text{SCN})_2]$, the linkage of SCN and Pd is through S.

5. (a) : $\text{Mn}^{7+} + 3e^- \longrightarrow \text{Mn}^{4+}$; $\text{Mn}^{7+} + 5e^- \longrightarrow \text{Mn}^{2+}$
 $\text{Mn}^{7+} + 4e^- \longrightarrow \text{Mn}^{3+}$; $\text{Mn}^{7+} + e^- \longrightarrow \text{Mn}^{6+}$

6. (c) : CO and CN^- are strong field ligands and force electrons to pair up so that a diamagnetic, low spin complex is resulted. However, Cl^- is a weak field ligand and hence does not force electrons to pair up so that a paramagnetic high spin complex results.

7. (c)

8. (d) : V^- can have better back bonding with vacant *p*-orbital of carbon in carbonyl, thus carbon and oxygen interaction (donation of electron) will be the least, thus bond order will be the lowest.

9. (b) : Magnetic moment, $\mu = 3.87$ B.M. corresponds to the number of unpaired electrons, $n = 3$.

10. (a)

11. Diamagnetic behaviour of Ti^{4+} is due to the absence of unpaired electrons.

$\text{Ti}(22) : [\text{Ar}]3d^24s^2$

$\text{Ti}^{4+} : [\text{Ar}]$

12. (i) Sodium hexafluoroaluminate(III)

(ii) Chlorobis(ethylenediamine) nitrito-O-cobalt(III) chloride

13. Mn shows the highest number of oxidation states, i.e., +2, +3, +4, +5, +6 and +7.

14. In a free transition metal ion, all the five *d*-orbitals are degenerate but when it is involved in a complex formation, the degeneracy is split. This is called crystal field splitting.

15. Lanthanum oxide (La_2O_3)

16. The ligands with small value of CFSE (Δ_o) are called weak field ligands whereas those with large value of CFSE are called strong field ligands.

17. E.C. of Zn = $[\text{Ar}]3d^{10}4s^2$. After loss of $2e^-$ to form Zn^{2+} , it acquires stable electronic configuration of $3d^{10}$ (fully-filled). Hence, it shows oxidation state of +2 only.

18. Here, 3 ions will be produced.

$\text{Co}(\text{NH}_3)_6\text{Cl}_2 \longrightarrow [\text{Co}(\text{NH}_3)_6]^{2+} + 2\text{Cl}^-$

19. Actinoids exhibit greater range of oxidation states than lanthanoids. This is because there is less energy difference between 5*f*, 6*d* and 7*s* orbitals in actinoids than the energy difference between 4*f*, 5*d* and 6*s* orbitals in case of lanthanoids. Hence, all their electrons can take part in bond formation.

20. The *trans*-isomer does not show optical isomerism as molecule has a plane of symmetry.

21. The atomic number of copper is 29. So, its outer shell electronic configuration is $3d^{10}4s^1$. Thus, Cu(I) ion has the configuration, $3d^{10}4s^0$.

Here all the electrons are paired. So, Cu(I) is diamagnetic. The outer shell electronic configuration of Cu(II) is $3d^9$. Here one unpaired electron is present in Cu(II) ion. As a result, Cu(II) ion is paramagnetic in nature.

22. $[\text{Co}(\text{NH}_3)_3\text{Cl}_3] < [\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl} <$

$[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2 < [\text{Co}(\text{NH}_3)_6]\text{Cl}_3$.

This is because number of ions produced from these complexes are 0, 2, 3 and 4 respectively. Therefore, as the number of ions increases, electrical conductivity increases.

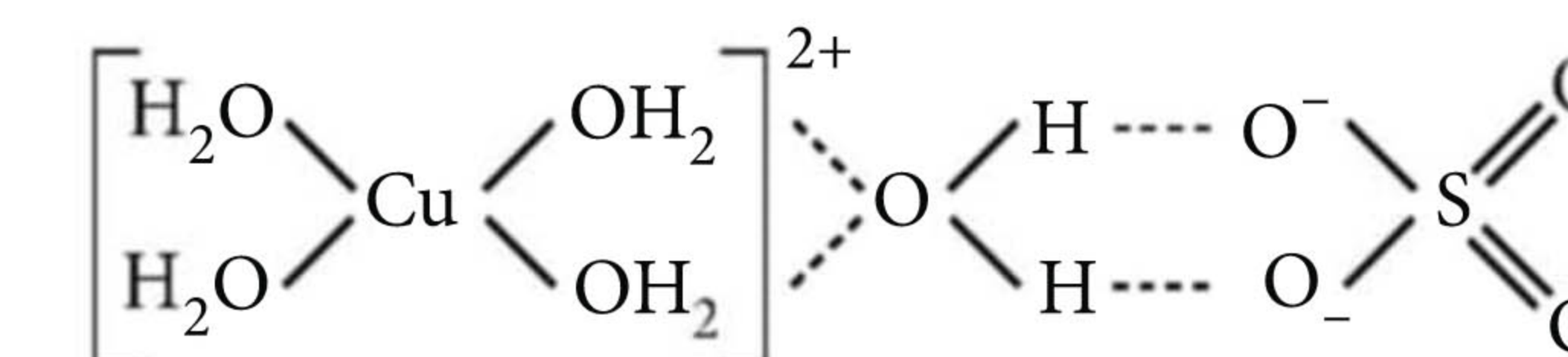
OR

$[\text{Co}(\text{CN})_6]^{3-}$ is an inner orbital or low spin complex involving the hybridisation d^2sp^3 while $[\text{CoF}_6]^{3-}$ is an outer orbital or high spin complex involving sp^3d^2 hybridisation.

23. (i) $8\text{MnO}_4^{-(aq)} + 3\text{S}_2\text{O}_3^{2-(aq)} + \text{H}_2\text{O}_{(l)} \longrightarrow$
 $8\text{MnO}_{2(aq)} + 6\text{SO}_4^{2-(aq)} + 2\text{OH}^{-(aq)}$

(ii) $\text{Cr}_2\text{O}_7^{2-(aq)} + 14\text{H}^{+(aq)} + 6\text{Fe}^{2+(aq)} \longrightarrow 2\text{Cr}^{3+(aq)} + 6\text{Fe}^{3+(aq)} + 7\text{H}_2\text{O}_{(l)}$

24. In copper sulphate pentahydrate, four water molecules are attached with Cu^{2+} and form $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$ ion which is blue in colour. In this complex, Cu^{2+} has one unpaired electron ($3d^9$) which shows $d \rightarrow d$ transition.



Structure of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$

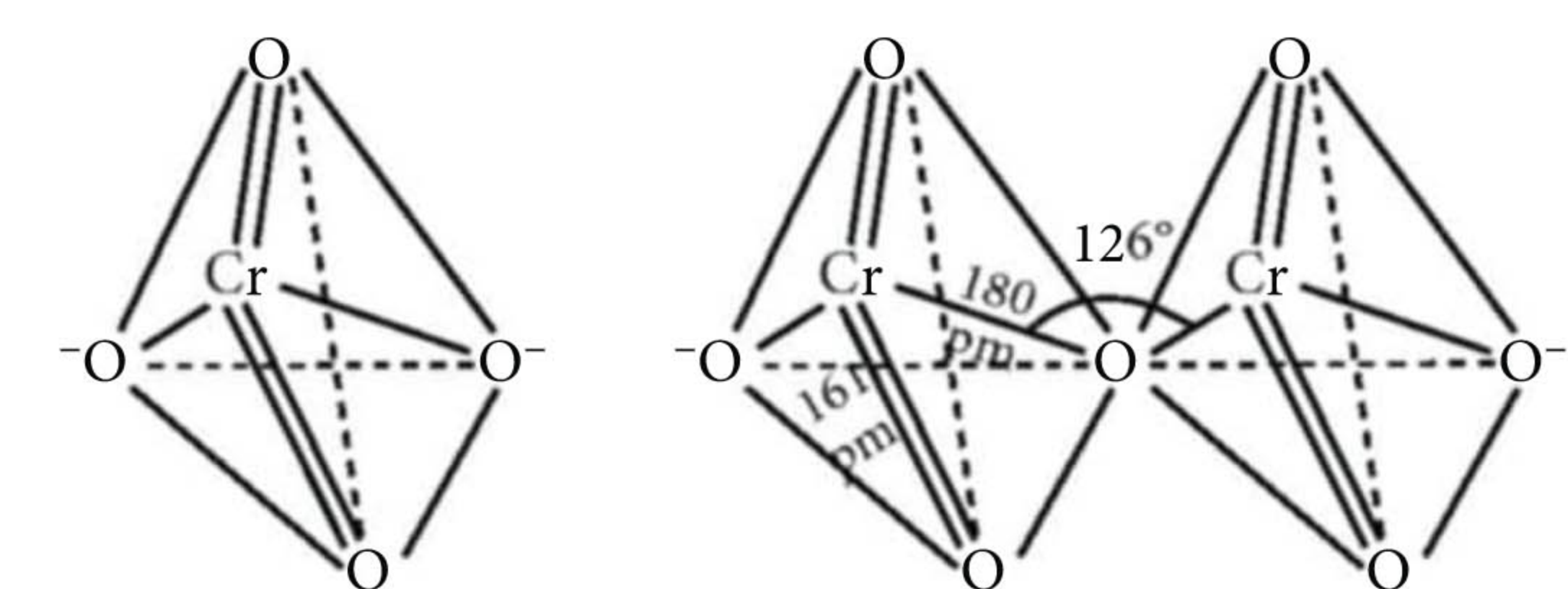
25. (i) Chromic sulphate is formed.

$\text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4 + 3\text{SO}_2 \longrightarrow$
 $\text{K}_2\text{SO}_4 + \text{Cr}_2(\text{SO}_4)_3 + \text{H}_2\text{O}$

(ii) Mohr's salt is oxidised to ferric sulphate.

$\text{K}_2\text{Cr}_2\text{O}_7 + 7\text{H}_2\text{SO}_4 + 6\text{FeSO}_4 \longrightarrow$
 $3\text{Fe}_2(\text{SO}_4)_3 + \text{Cr}_2(\text{SO}_4)_3 + \text{K}_2\text{SO}_4 + 7\text{H}_2\text{O}$

OR



Tetrahedral
Structure of CrO_4^{2-}

Structure of $\text{Cr}_2\text{O}_7^{2-}$
(Two tetrahedral units join together)

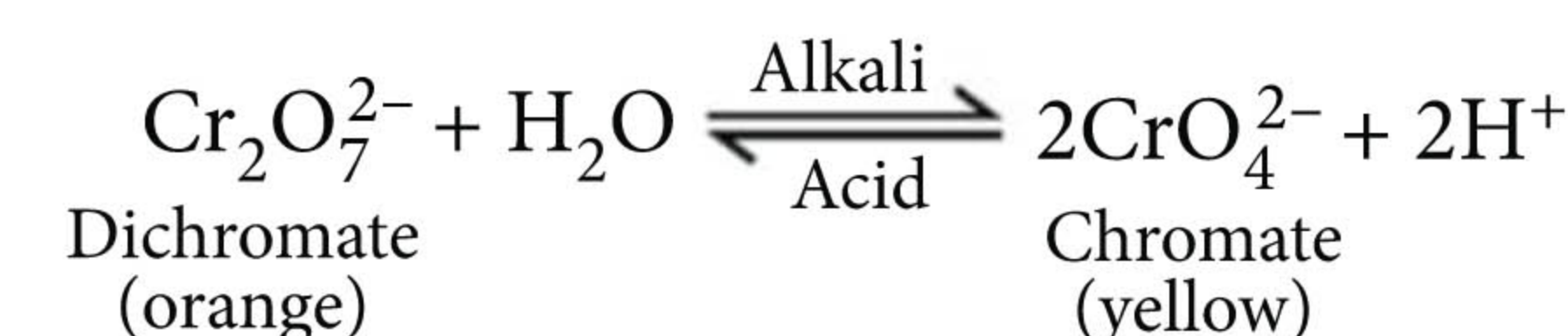
26. Magnetic moment μ , can be calculated with the help of following relation, $\mu = \sqrt{n(n+2)}$ B.M.

where, n is the number of unpaired electrons in the ion or atom and B.M. is Bohr Magneton (unit of magnetic moment).

If any ion contains two unpaired electron (e.g., Ti^{2+}) the magnetic moment will be 2.82 B.M.

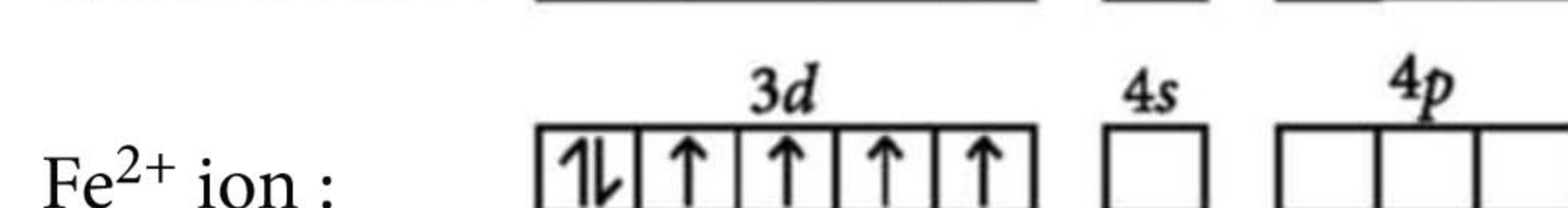
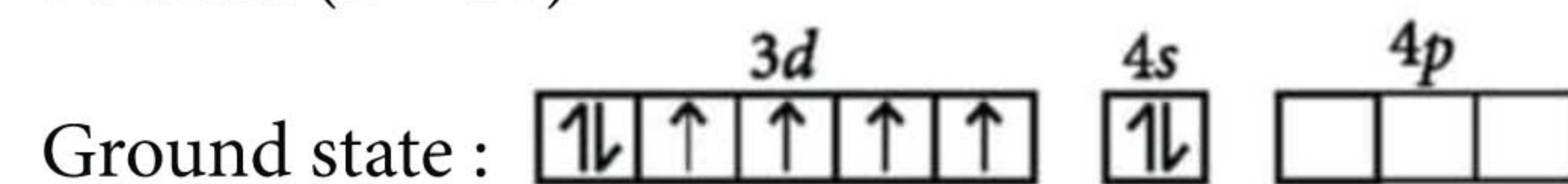
$$\mu = \sqrt{2(2+2)} = \sqrt{8} = 2.82 \text{ B.M.}$$

27. At lower pH, the colour of the solution is orange due to the presence of dichromate ions ($\text{Cr}_2\text{O}_7^{2-}$). But in alkaline pH (on increasing pH), the colour of the solution changes to yellow due to the conversion of dichromate ions to chromate ions.

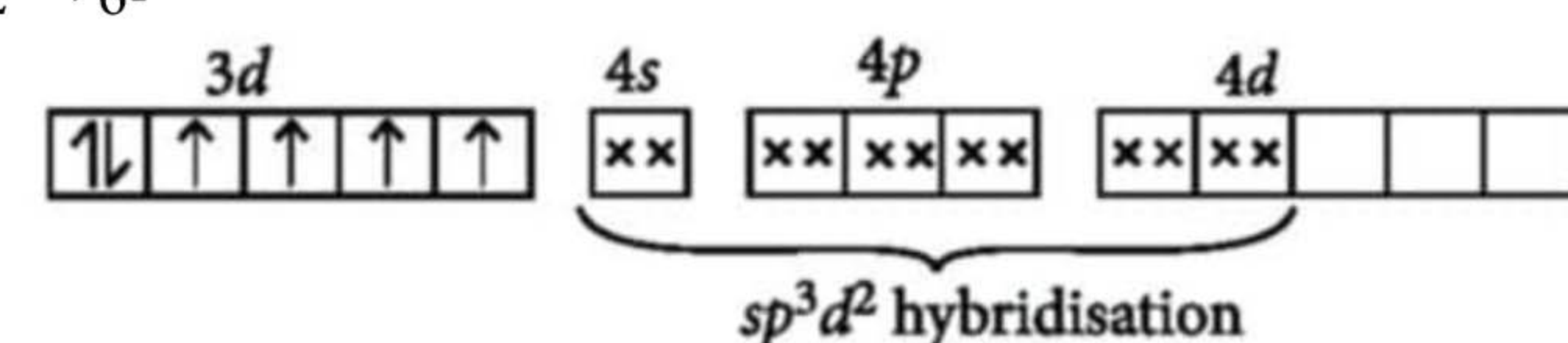


28. (i) In $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$:

Fe atom ($Z = 26$)



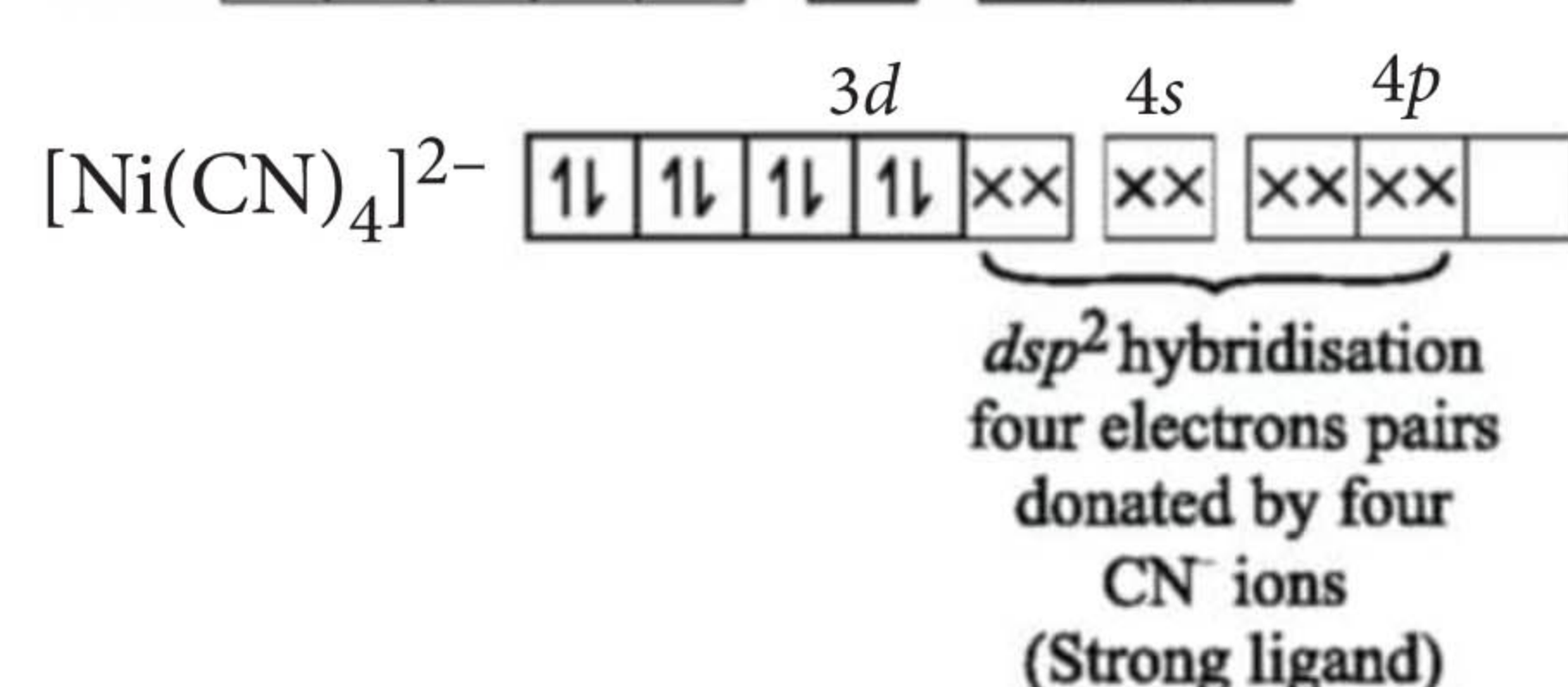
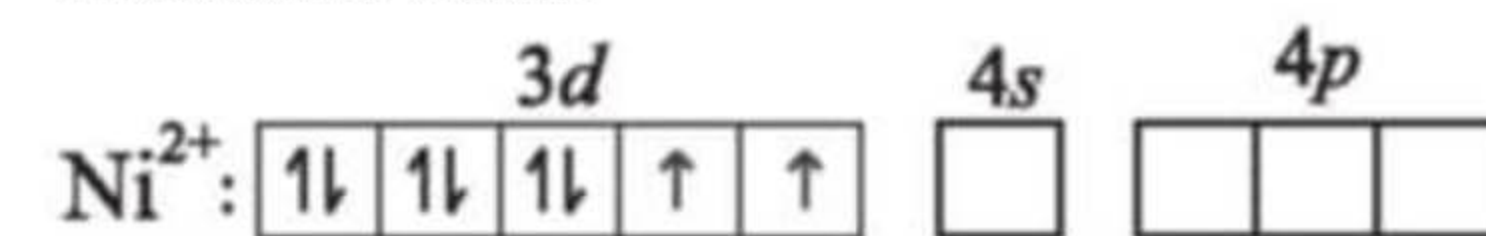
$[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$:



The Fe^{2+} ion has outer orbital octahedral geometry (high spin) with sp^3d^2 hybridisation. This complex is paramagnetic due to the presence of four unpaired electrons.

(ii) In $[\text{Ni}(\text{CN})_4]^{2-}$: Ni(28) is present as Ni(II) with $3d^8$ configuration.

Ground state

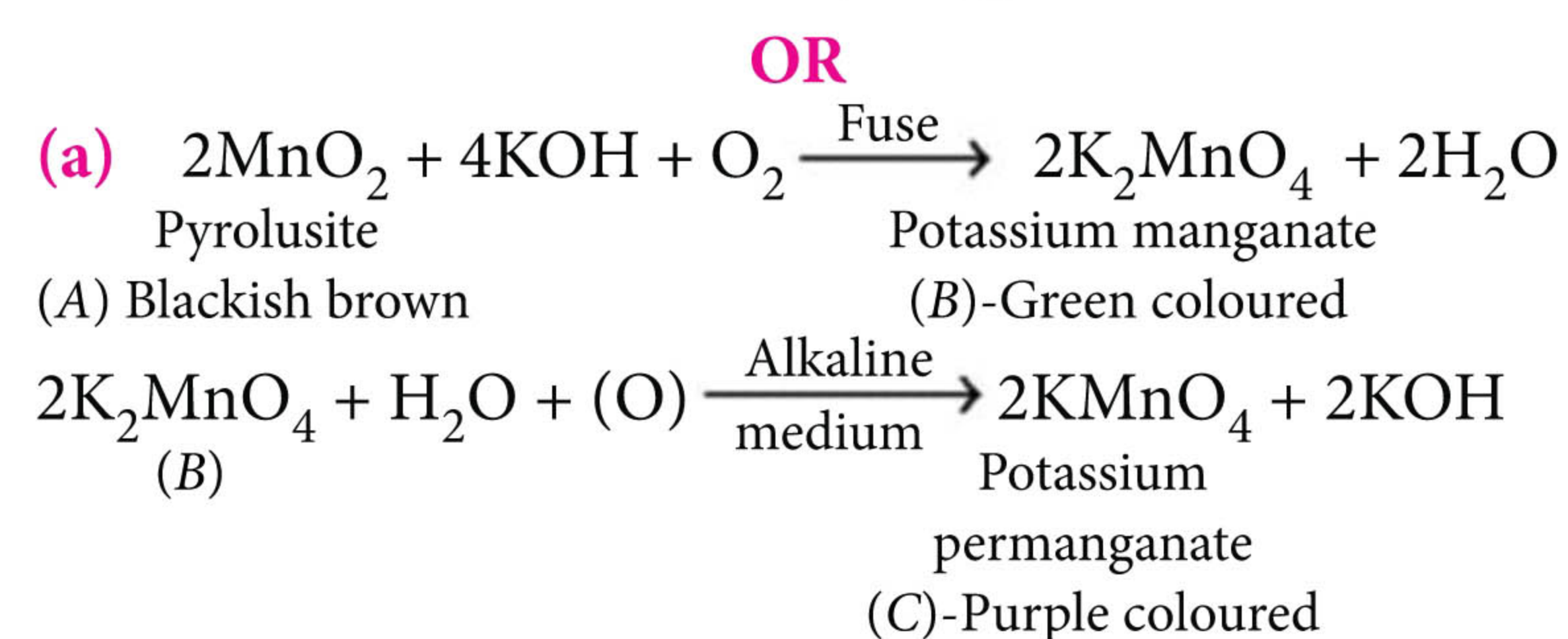


The complex ion has square planar geometry and is diamagnetic in nature.

29. (i) This is due to increasing stability of the lower species to which they are reduced.

(ii) This is due to poor shielding effect of 5f electrons of actinoids than 4f electrons of lanthanoids.

(iii) This is due to high electronegativity and multiple bond formation with metal by oxygen.



or $\text{MnO}_4^{2-} \longrightarrow \text{MnO}_4^- + e^-$

(b) When acidic solution of green compound (B), i.e., potassium manganate is allowed to stand for some time, it disproportionates to give permanganate as follows:



This reaction is called disproportionation reaction.

30. (i) Coordination number of central metal ion (Fe^{3+}) is six.

(ii) Following factors affect the stability of the complexes:

(a) Basic nature of the ligand: Greater the basic nature of the ligand greater will be the stability. The copper complex with CN^- is more stable than the complex with NH_3 (less basic).

(b) Charge on central metal ion: Greater the charge on central metal ion greater will be the stability. $[\text{Fe}(\text{CN})_6]^{3-}$ is more stable than $[\text{Fe}(\text{CN})_6]^{4-}$ due to the higher charge on Fe.

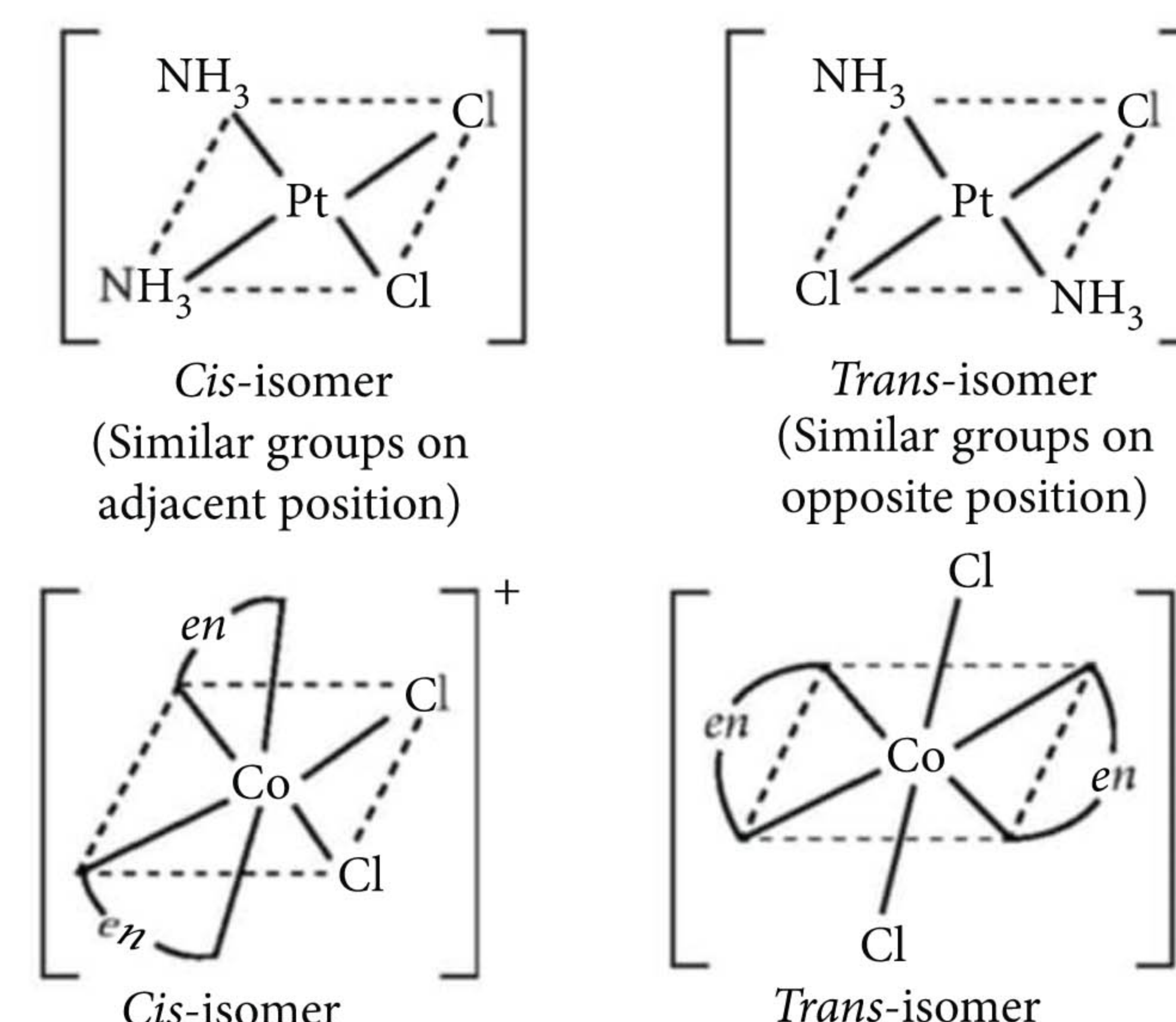
(c) Number of ring structures (chelate ring) in complex: If a ring is formed in a complex, it provides extra stability. Thus, chelates are more stable.

OR

Cis and *trans*- isomerism i.e., geometrical isomerism arises due to the different arrangement of ligands around the central metal ion. In *cis* (in Latin *cis* means same) isomer two identical ligand molecules are adjacent to each other i.e., on same side of central metal while in *trans* (in Latin *trans* means across) isomer two identical ligand molecules are diametrically opposite to each other.

These two isomers differ in physical and chemical properties of each other and can be separated by some chemical and physical methods. This type of isomerism is not found in tetrahedral complexes but is common in square planar and octahedral complexes.

Example: $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$, $[\text{Co}(\text{en})_2\text{Cl}_2]^+$

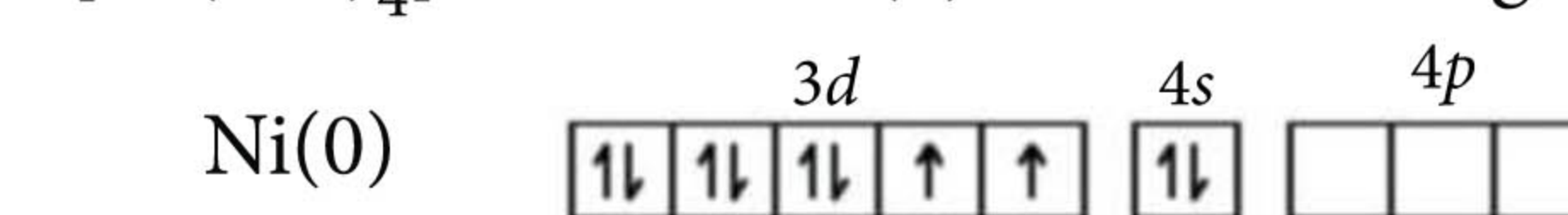


31. (i) Manganese can form $p\pi - d\pi$ bond with oxygen by utilising $2p$ -orbital of oxygen and $3d$ -orbital of manganese due to which it can show highest oxidation state of +7. While with fluorine it cannot form such $p\pi - d\pi$ bond thus, it can show a maximum of +4 oxidation state.

(ii) Mn^{3+} has a d^4 -configuration, so it has greater tendency to accept one electron to acquire d^5 configuration. On the other hand, Fe^{3+} has a d^5 configuration which is more stable than the d^6 configuration of Fe^{2+} . As a result, reduction of Fe^{3+} to Fe^{2+} is not favoured. Since, E° values reflect the reduction tendency therefore, E° value for $\text{Mn}^{3+}/\text{Mn}^{2+}$ couple is more positive than $\text{Fe}^{3+}/\text{Fe}^{2+}$.

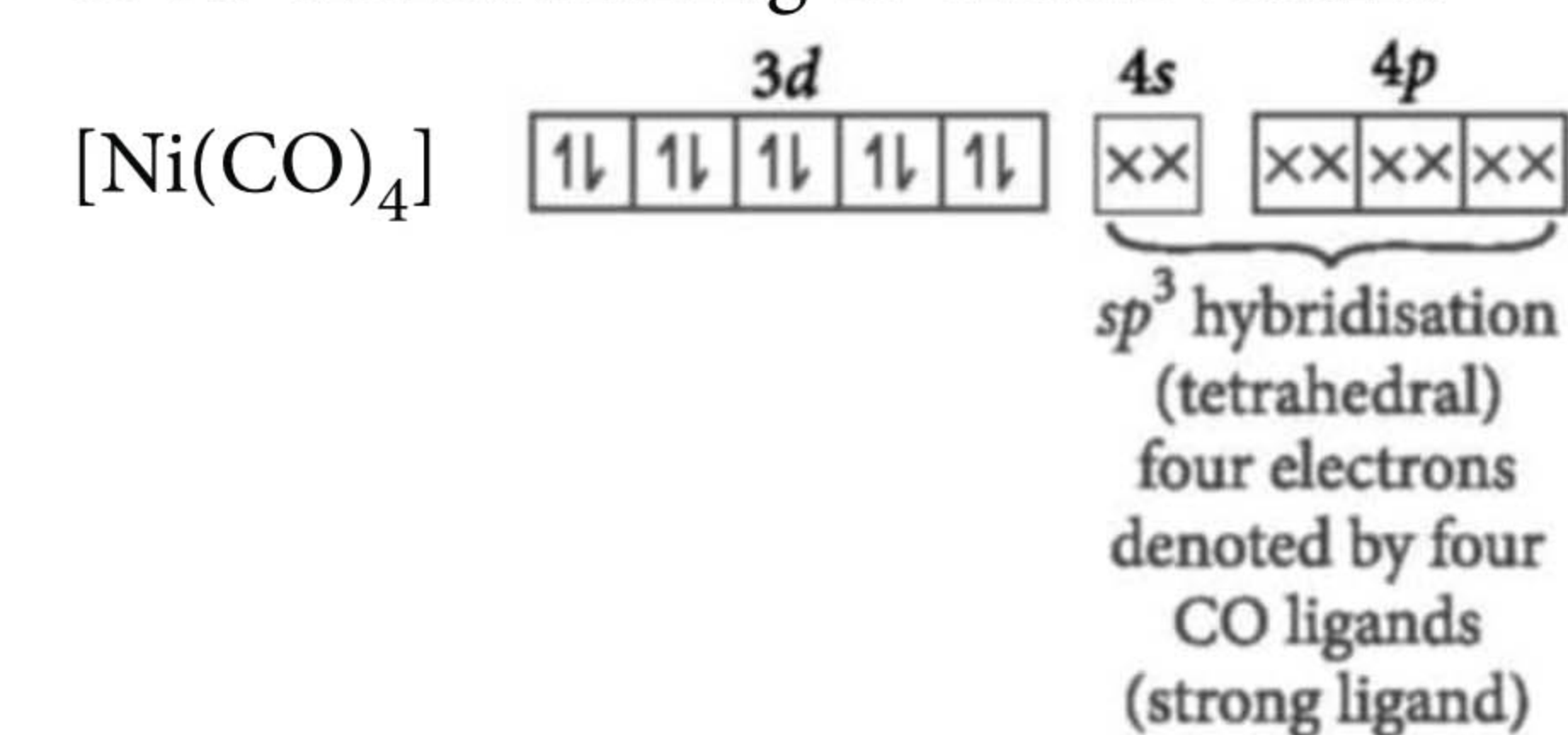
(iii) The transition elements form a number of interstitial compounds in which atoms of light elements such as H, C and N occupy the voids in their lattices. The products obtained in this way are hard and rigid. For example, steel and cast iron become hard due to the formation of an interstitial compound with carbon.

32. The electronic configuration of Ni^{2+} is $[\text{Ar}]3d^84s^0$. $[\text{Ni}(\text{CO})_4]$ contains Ni(0) – $3d^84s^2$ configuration.



Ground state

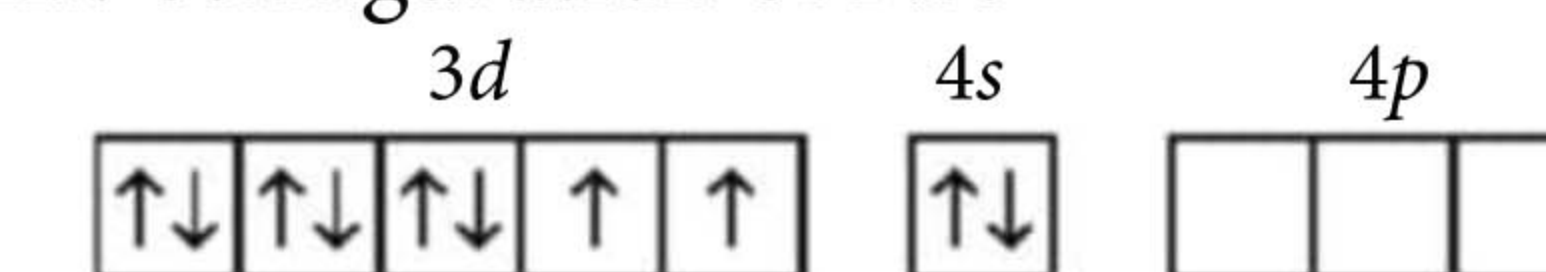
CO is a strong field ligand hence, $4s$ -electrons will shift to $3d$ -orbital making $4s$ -orbital vacant.



The complex has all paired electrons hence, it is diamagnetic.

$[\text{NiCl}_4]^{2-}$: Cl^- is a weak field ligand. Formation of $[\text{NiCl}_4]^{2-}$ is shown below:

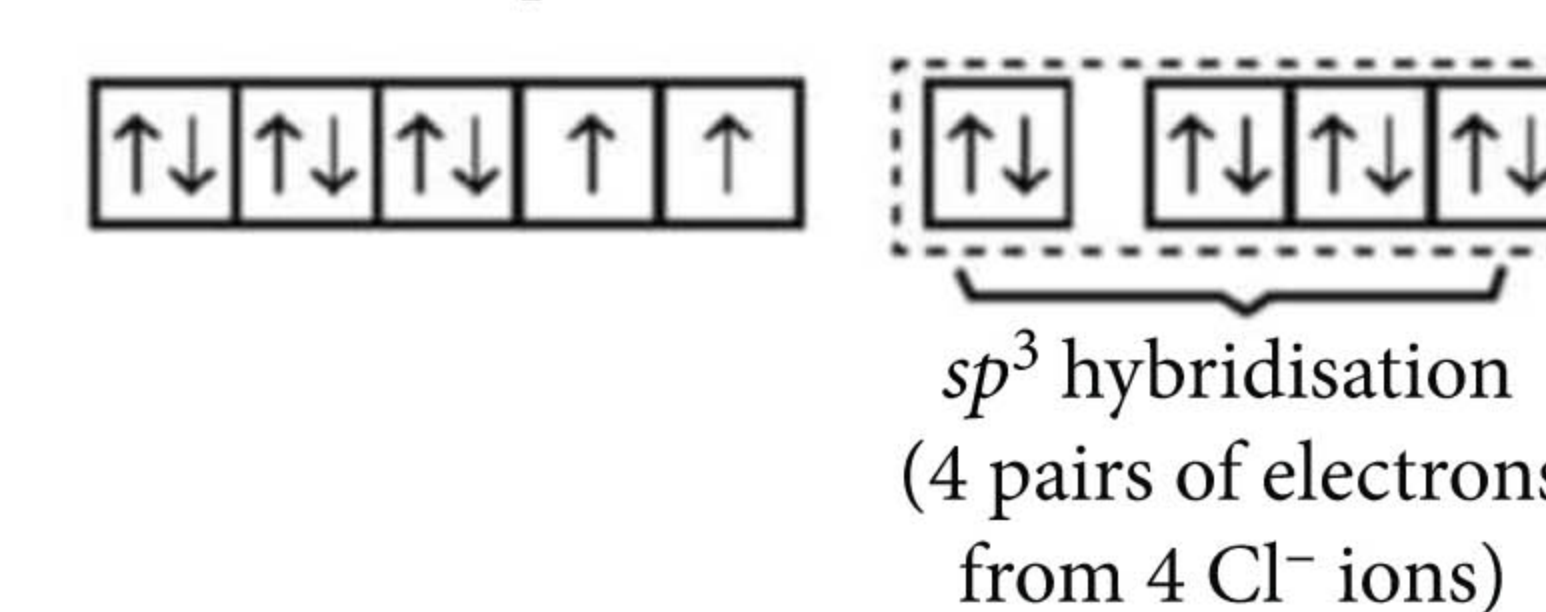
Electronic configuration of Ni:



Electronic configuration of Ni^{2+} (ground state):



Formation of $[\text{NiCl}_4]^{2-}$:



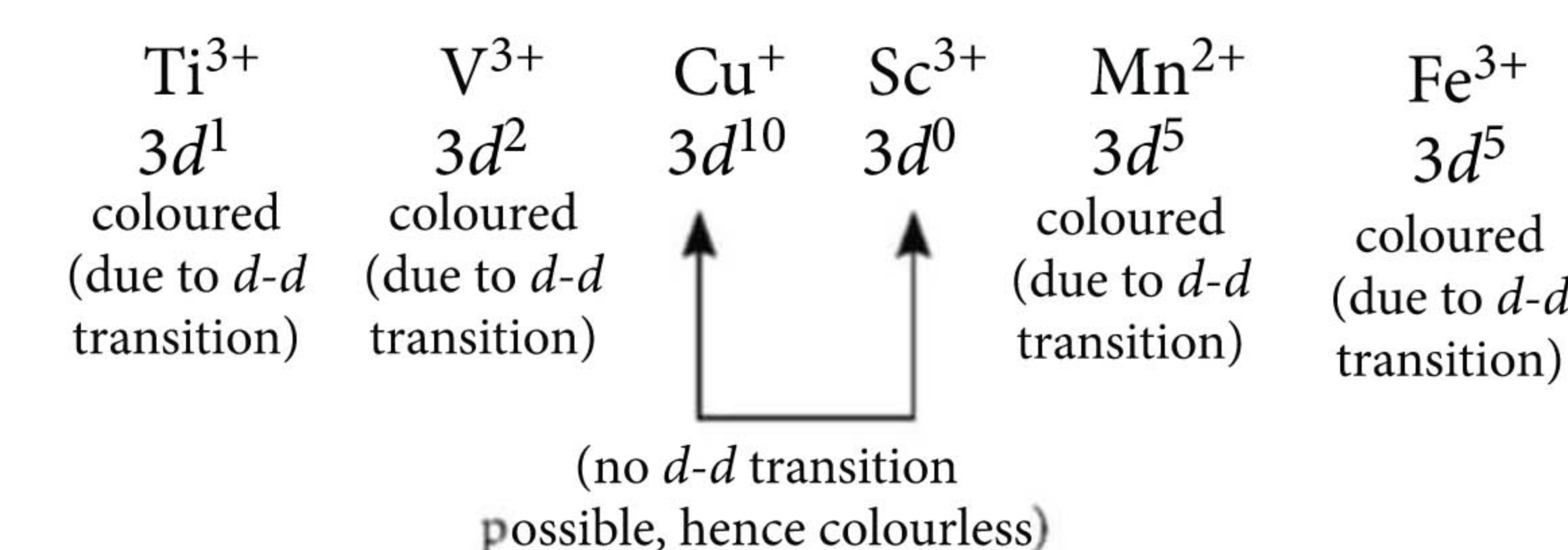
Since, there are two unpaired electrons in $[\text{NiCl}_4]^{2-}$, it is paramagnetic.

Magnetic moment of $[\text{NiCl}_4]^{2-}$,

$$\mu = \sqrt{2(2+2)} = \sqrt{8} \text{ B.M.} = 2.83 \text{ B.M.}$$

Shape of $[\text{NiCl}_4]^{2-}$: Tetrahedral

33. The outer electronic configurations of the given ions are



GLIMPSE OF NEXT ISSUE...

- CBSE Warm Up (XII)
- Haloalkanes & Haloarenes
- Alcohols, Phenols & Ethers
- Brush Up for NEET/JEE (XII)
- The d- & f-Block Elements
- Coordination Compounds
- Brush Up for NEET/JEE (XI)
- Equilibrium
- Redox Reactions
- Monthly Test Drive (XI)
- Hydrogen
- s-Block Elements

34. Octahedral complex :

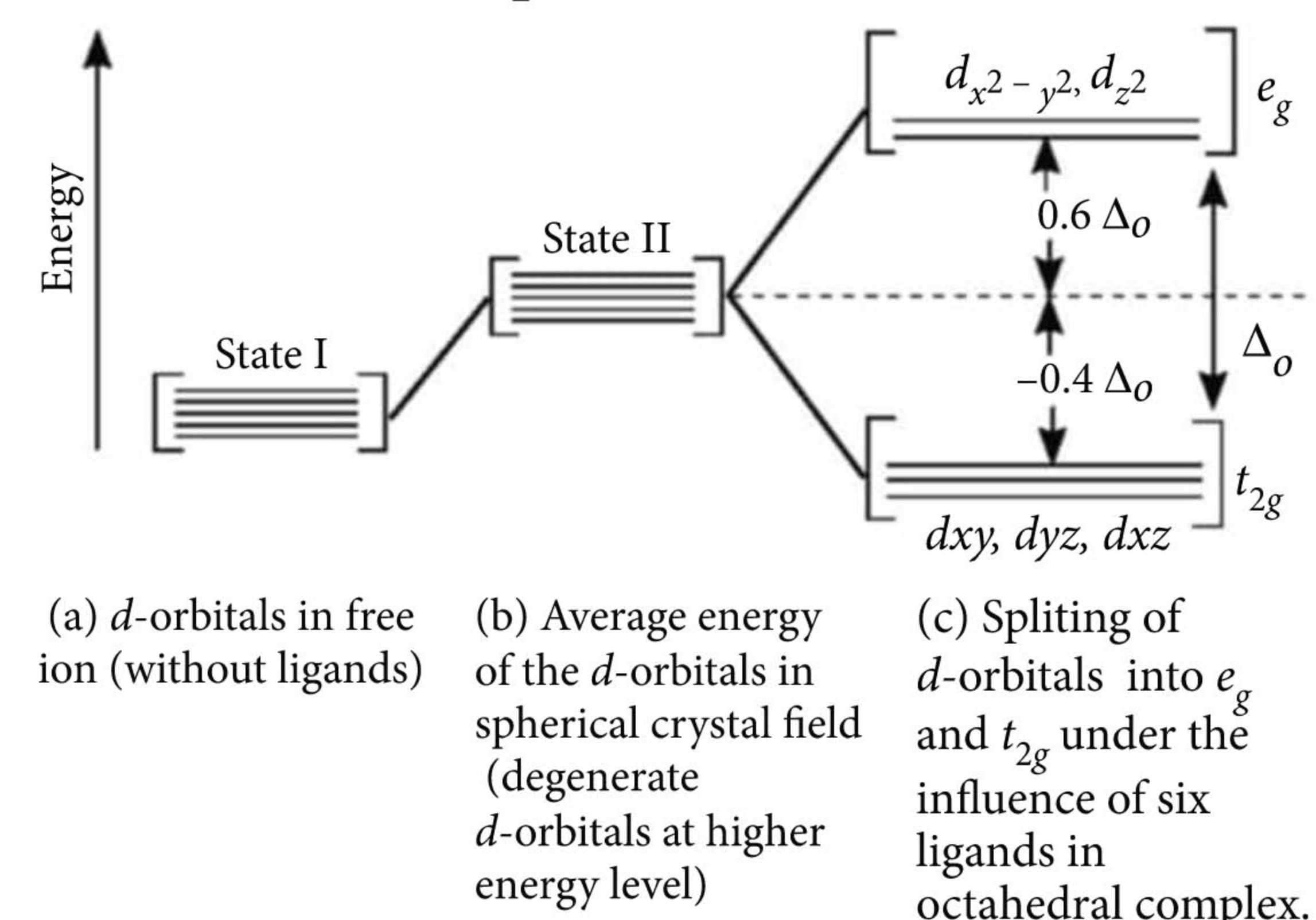


Fig.: Splitting of five d -orbitals in octahedral complex.

Tetrahedral complex:

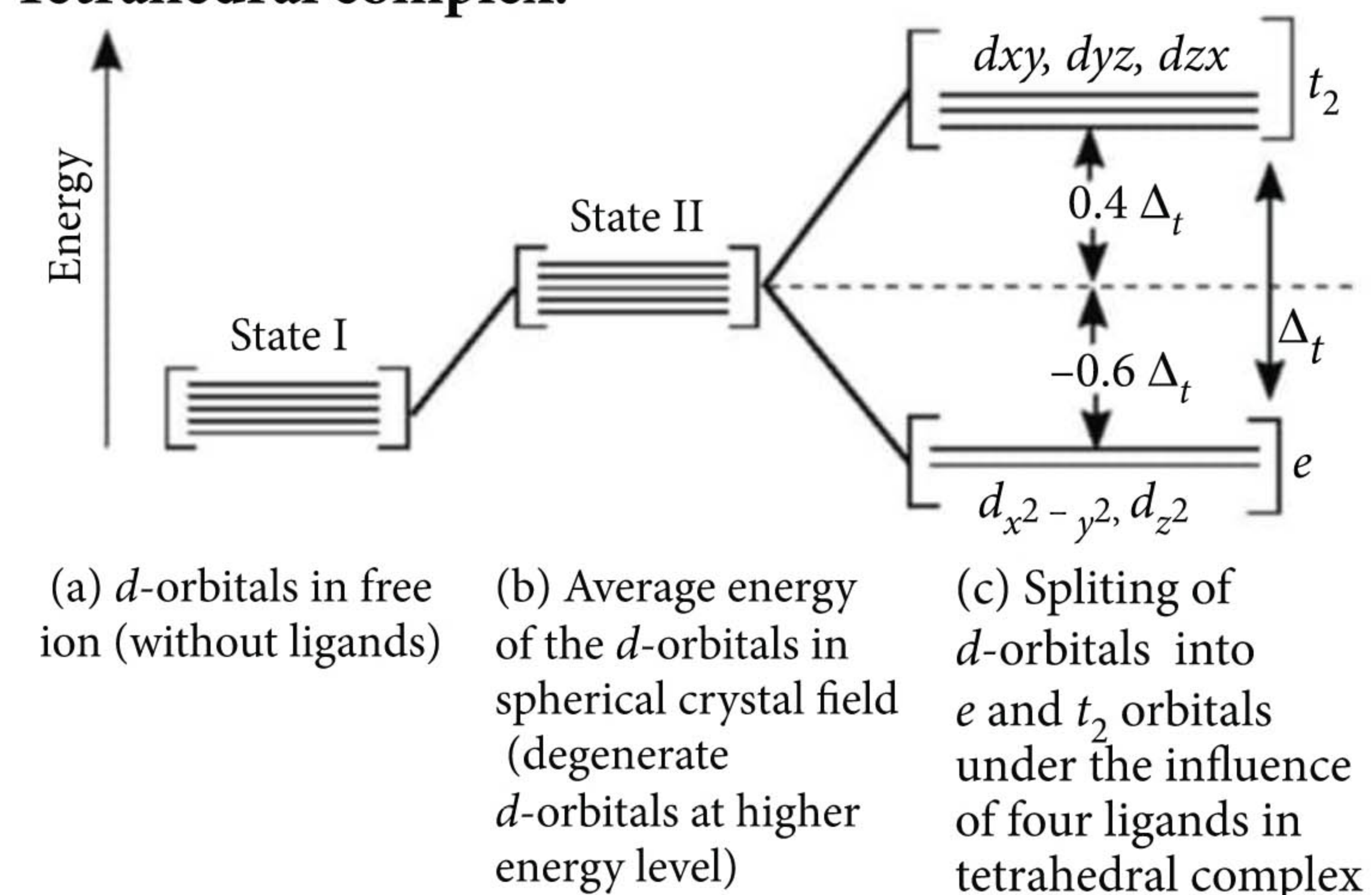


Fig.: Splitting of five d -orbitals in tetrahedral complex.

35. (a) Metallic character : Since the number of electrons in the outermost shell are two or one and can be removed easily. Therefore, all the transition elements are metals. All three types of structures : *fcc*, *hcp* and *bcc* are shown by them. The electrons present in the outermost orbitals form metallic bonds. Due to these metallic bonds they have high melting and boiling points and high thermal and electrical conductivities. All transition metals except Hg are malleable and ductile.

(b) Ionisation energy : The first ionisation energies of transition elements lie between the value of ionisation energies of s -block and p -block elements. In transition elements last electron goes to $(n-1)d$ sub-shell which shields the outer ns -electrons from the inward pull due to the attraction by the nucleus. The nuclear charge and shielding effect of $(n-1)d$ electrons will increase with the increase in atomic number. The ionization energies gradually increase in a particular series of d -block elements. This is due to decrease in size with

the increase in atomic numbers which will make the removal of electrons difficult. However, shielding effect will also increase with the increase in atomic number which will oppose the decrease in size. Due to these two opposing effects (increased nuclear charge and shielding effect), ionisation energies will increase rather slowly in the $3d$ -series.

(c) Variable oxidation state : Transition elements show variable oxidation states, because the energy of ns orbitals is very close to the energies of $(n-1)d$ orbitals, therefore, the electrons of ns and $(n-1)d$ orbitals can be used for bond formation.

About the oxidation states following points should be noted:

(i) In transition elements, +1 is the minimum oxidation state (shown by Cr, Cu, Ag, Hg) and +8 is the maximum oxidation state (shown by Ru and Os). Zero oxidation state is found only in complexes.

(ii) The transition elements in lower oxidation states form ionic bonds, while in higher oxidation states form covalent bonds, e.g., in CrO_4^{2-} (chromate ion) all the bonds are covalent in nature.

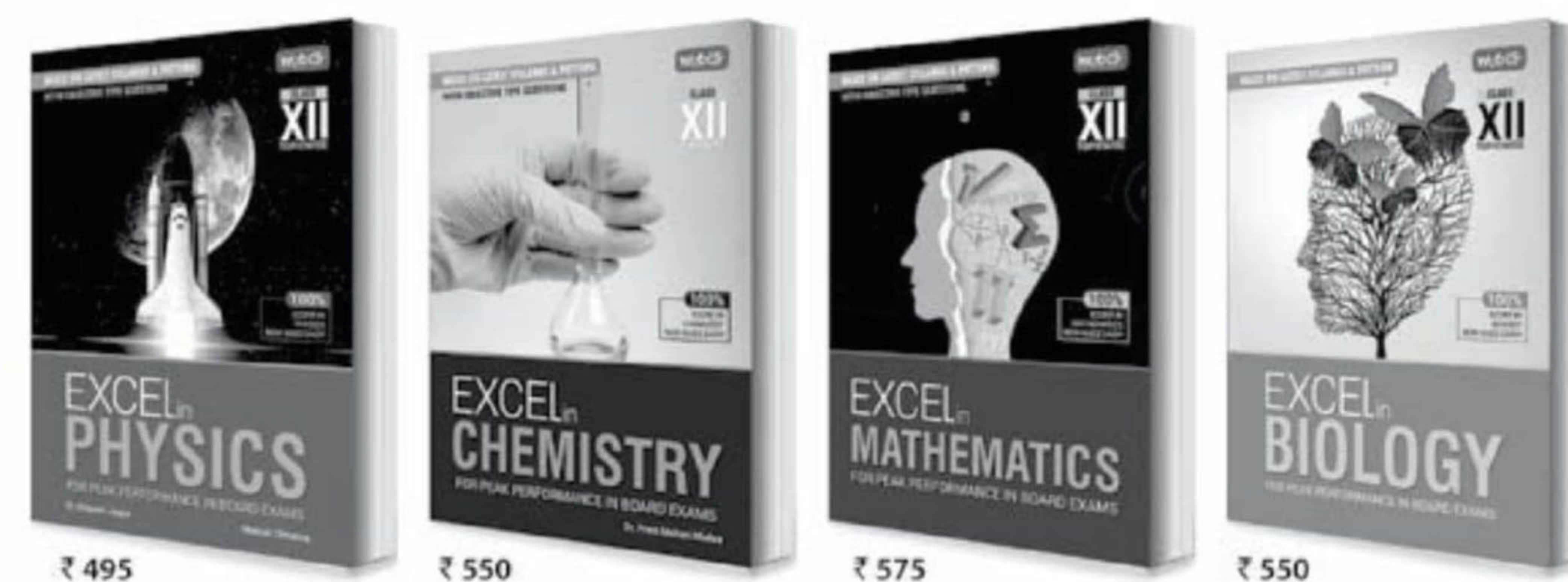
(iii) In first transition series if any oxidation state has 0, 5 or 10 electrons in d -subshell then that oxidation state will be more stable, e.g., Ti^{4+} ($3d^0$) is more stable than Ti^{3+} ($3d^1$), Mn^{2+} ($3d^5$) is more stable than Mn^{3+} ($3d^4$).

OR

(i)

Property	Lanthanoids	Actinoids
(a) Electronic configuration	$4f^{1-14} 5d^{0-1} 6s^2$	$5f^{1-14} 6d^{0-1} 7s^2$
(b) Oxidation states	+2, +3 and +4. The +3 state is the most stable.	The dominant oxidation state is +3. Actinoids also show higher oxidation states. The maximum oxidation state first increases upto the middle of the series and then decreases.
(c) Atomic and ionic sizes	The atomic and the ionic sizes decrease steadily in going from Ce to Lu.	The atomic and ionic (M^{3+}) sizes decrease gradually across the series.

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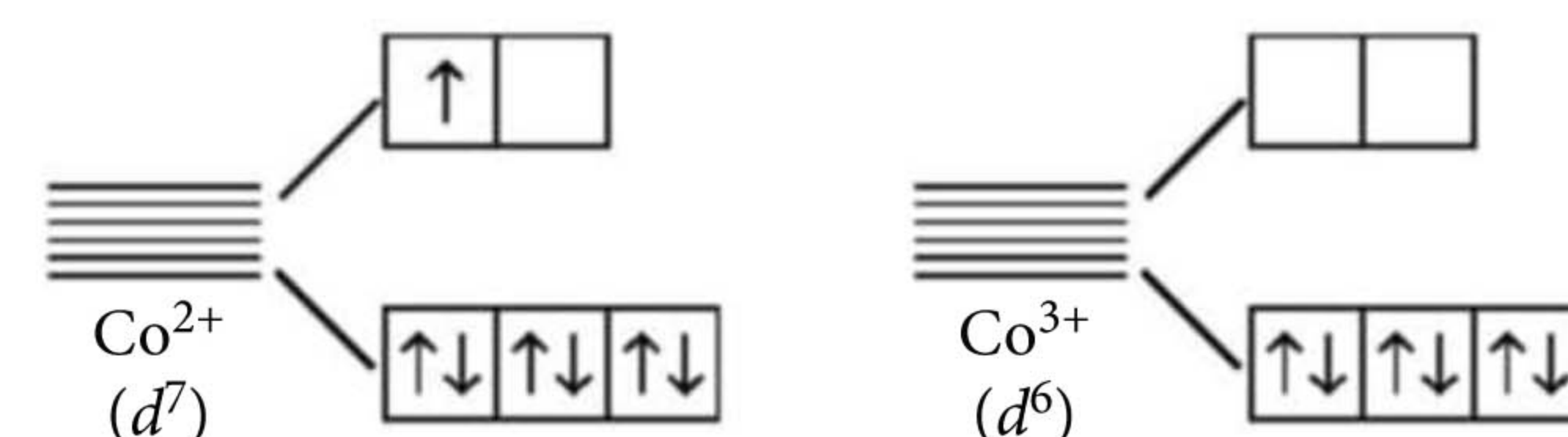


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(ii) (a) The $E^\circ_{\text{Cr}^{3+}/\text{Cr}^{2+}}$ is -0.41 V. Therefore, the tendency for Cr^{2+} to form Cr^{3+} by releasing one electron is higher. Thus, Cr^{2+} is strongly reducing agent.

The Mn^{3+} (d^4 configuration) acts as a strongly oxidising agent as it can revert to Mn^{2+} (d^5 configuration) in the process. Mn^{2+} has half-filled d -orbitals, which impart greater stability to Mn^{2+} ion. The E° value for $\text{Mn}^{3+} + e^- \rightarrow \text{Mn}^{2+}$ is $+1.57$ V.

(b) Cobalt (II) has $3d^7$ and cobalt (III) has $3d^6$. In the presence of complexing agent, the crystal field stabilization energy of Co^{3+} (having $3d^6$ configuration) is higher than that for Co^{2+} (having $3d^7$ configuration). Therefore, in the presence of complexing agent, Co^{2+} gets easily oxidised to Co^{3+} .



36.

Complex and IUPAC name	Oxidation state of central metal ion/atom	Electronic configuration of central metal ion/atom (outer)	Coordination number	Geometry	Magnetic moment (B.M.)
(a) $\text{K}[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$ potassium diaquabis(oxalto)chromate(III) trihydrate	+3	$3d^3$ or t_{2g}^3	6	Octahedral	3.87
(b) $[\text{CrCl}_3(\text{py})_3]$ trichloridotripyridinechromium(III)	+3	$3d^3$ or t_{2g}^3	6	Octahedral	3.87
(c) $\text{K}_4[\text{Mn}(\text{CN})_6]$ potassium hexacyanomanganate(II)	+2	$3d^5$ or t_{2g}^5	6	Octahedral	1.73
(d) $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ pentaamminechloridocobalt(III) chloride	+3	$3d^6$ or t_{2g}^6	6	Octahedral	0
(e) $\text{Cs}[\text{FeCl}_4]$ caesium tetrachloridoferrate(III)	+3	$3d^5$ or $e^2 t_2^3$	4	Tetrahedral	5.92

OR

(i) This theory is given by Pauling. The main assumptions of this theory are as follows :

(a) The empty s , p and d atomic orbitals equal to the coordination number of central metal ion, are made available by the central metal atom or ion. The vacant orbitals get hybridized to produce equal number of hybridized orbitals of same energy and shape which are arranged in definite geometry.

(b) The ligand molecules must have at least one σ -orbital containing a lone pair of electrons.

(c) These σ -orbitals (containing lone pairs) of ligand are overlapped by the vacant hybridized orbitals of metal atoms or ions to form ligand \rightarrow Metal σ -bond (coordinate bond).

(ii) If the d -orbitals used in the hybridization (d^2sp^3) are of lower shell than the s - and p - orbitals *i.e.*, $(n-1)d$ then the complexes formed are called inner orbital or low spin complexes. For example in $\text{K}_4[\text{Fe}(\text{CN})_6]$, $3d$, $4s$ and $4p$ orbitals take part in hybridization, therefore, it is an inner orbital complex.

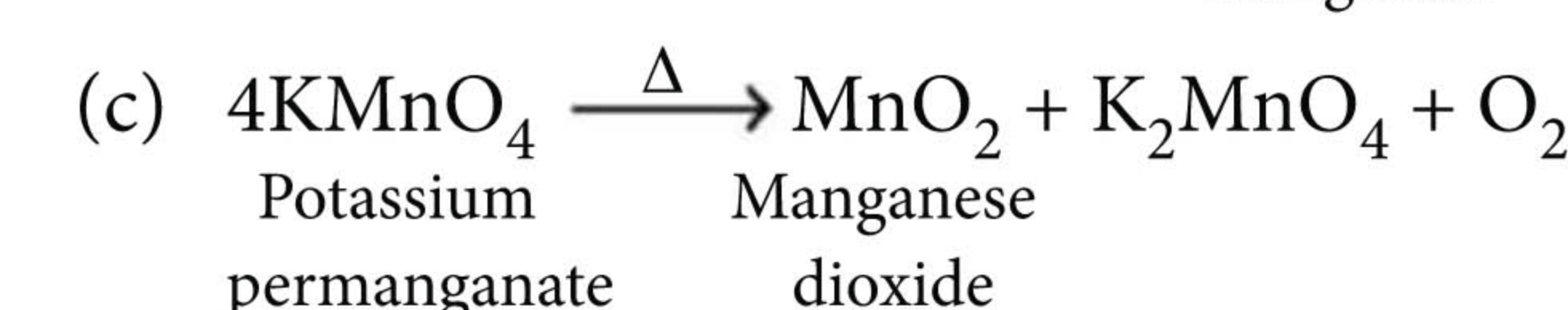
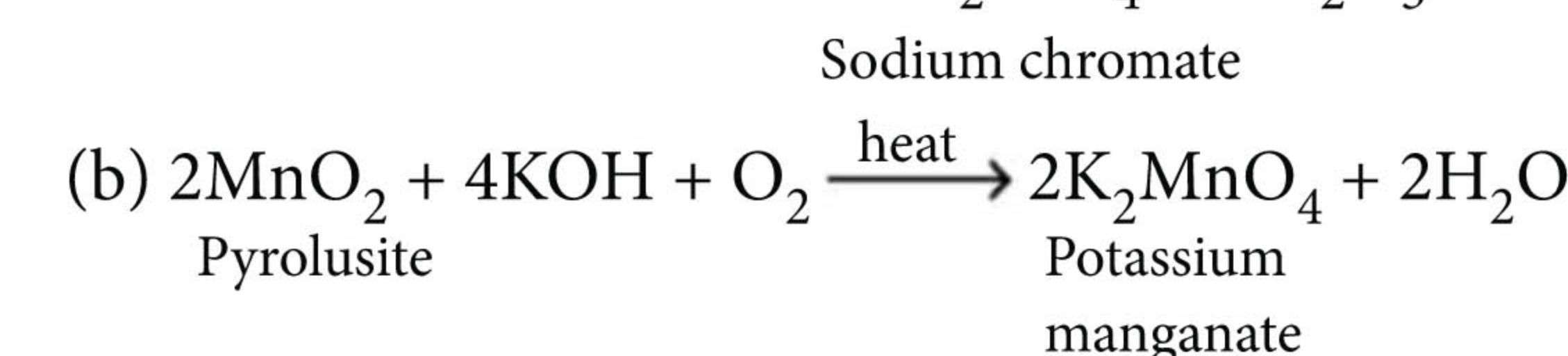
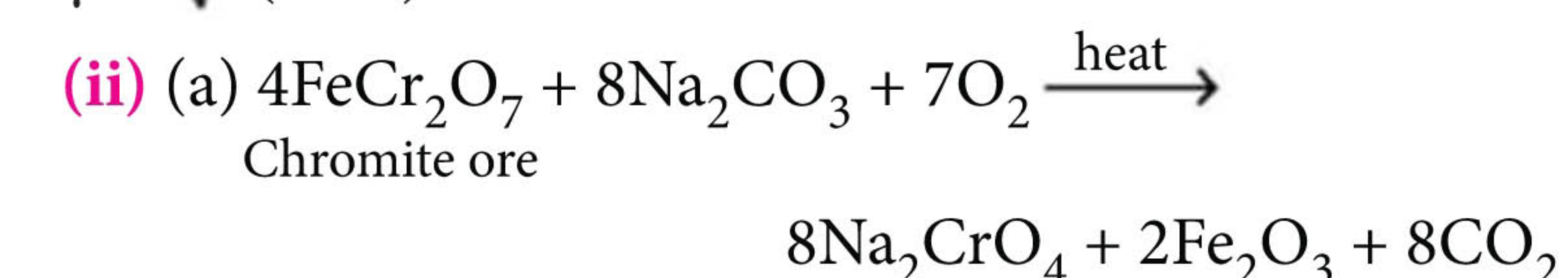
If the d -orbitals used in the hybridization (sp^3d^2) are of the same principal energy level as that of s - and p -orbitals, the complexes are called outer orbital complexes or high spin complexes. For example in $[\text{FeF}_6]^{3-}$, $4s$, $4p$ and $4d$ orbitals take part in hybridization, therefore, it is outer orbital complex.

37. (i) (a) Fe has higher melting point than Cu, because iron has four unpaired electrons in d -subshell ($3d^6 4s^2$), therefore, the metallic bonds and covalent

bonds in iron are stronger in Fe but in Cu ($3d^{10} 4s^1$) no d -electron is unpaired and only one $4s$ electron is responsible for metallic bond.

(b) Co^{2+} and Ni^{2+} have $3d^7 4s^0$ and $3d^8 4s^0$ configuration respectively, hence 3 unpaired electrons are present in Co^{2+} and 2 unpaired electrons are present in Ni^{2+} . Therefore, Ni^{2+} has lower magnetic moment, because it depends upon number of unpaired electrons *i.e.*,

$$\mu = \sqrt{n(n+2)}.$$



OR

The steady decrease in atomic and ionic radii of lanthanum ions as we move from La to Lu, is known as lanthanide contraction.

Cause : In lanthanides, last electron enters the $4f$ -sub-shell *i.e.*, second last shell. The shape of f -orbitals is very much diffused, because of this reason the mutual shielding of $4f$ -electrons is very little. The nuclear charge increases at each step due to the increase in atomic number, while the mutual shielding effect of $4f$ -electrons is comparatively negligible. This causes a decrease in size of the $4f$ sub-shell with the increase in atomic number.

Consequences : Following are the main consequences of lanthanide contraction:

(a) **Basic strength of oxides and hydroxides of lanthanides :** The basic strength of oxides and hydroxides of lanthanides decrease with the increase in atomic number. With the increase in atomic number the size of lanthanum ions (Ln^{3+}) decreases, due to lanthanide contraction. The decrease in size of Ln^{3+} , increases the covalent character *i.e.*, decreases the ionic character between Ln^{3+} and OH^- ions, consequently the basic strength of oxide and hydroxide will decrease.

(b) **Similar sizes of second and third transition series elements :** Normally the atomic radii increases with the increase in atomic number in the same subgroup, but in

lanthanides the atomic radii of the elements of second and third transition series are almost similar.

The expected increase in size from second to third transition series is cancelled by the decrease in size due to lanthanide contraction. Due to the similar atomic radii of second and third transition series elements, they resemble each other very closely.

(c) **Separation of Lanthanides :** The properties of lanthanides are very similar, therefore, it is difficult to separate them. However, due to lanthanide contraction, decrease in size of lanthanides make the separation possible by ion exchange methods.

For the
SCIENTIST in
YOU

Ultra-thin layers of rust generate electricity from flowing water!!!

There are many ways to generate electricity -- batteries, solar panels, wind turbines and hydroelectric dams, to name a few examples. And now there's rust.

New research conducted by scientists shows that thin films of rust *i.e.*, iron oxide, can generate electricity when saltwater flows over them. These films represent an entirely new way of generating electricity and could be used to develop new forms of sustainable power production. Interactions between metal compounds and saltwater often generate electricity, but this is usually the result of a chemical reaction in which one or more compounds are converted to new compounds. Reactions like these are what is at work inside batteries.

In contrast, the phenomenon discovered recently does not involve chemical reactions, but rather converts the kinetic energy of flowing saltwater into electricity.

The phenomenon, the electrokinetic effect, has been observed before in thin films of graphene, sheets of carbon atoms arranged in a hexagonal lattice and it is remarkably efficient. The effect is around 30 percent efficient at converting kinetic energy into electricity. For reference, the best solar panels are only about 20 percent efficient.

"A similar effect has been seen in some other materials. You can take a drop of saltwater and drag it across graphene and see some electricity generated," Scientist says.

However, it is difficult to fabricate graphene films and scale them up to usable sizes. The iron oxide films discovered, are relatively easy to produce and scalable to larger sizes, Scientist says.

MONTHLY TEST DRIVE



This specially designed column enables students to self analyse their extent of understanding of specified chapters. Give yourself four marks for correct answer and deduct one mark for wrong answer. Self check table given at the end will help you to check your readiness.

Aldehydes, Ketones and Carboxylic Acids / Organic Compounds

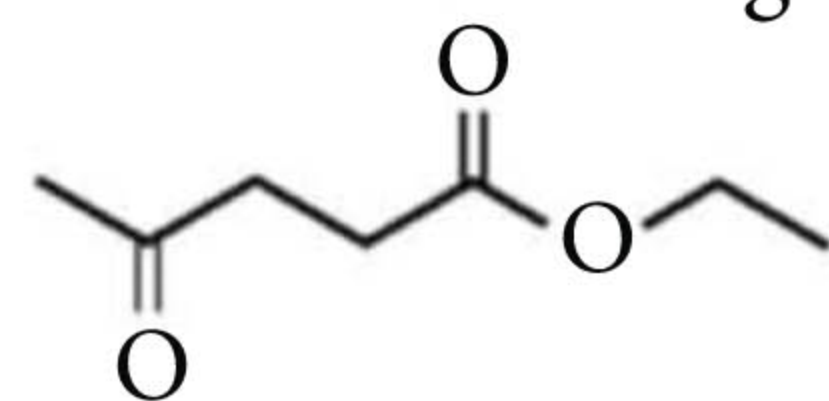
Total Marks : 120

Containing Nitrogen

Time Taken : 60 Min.

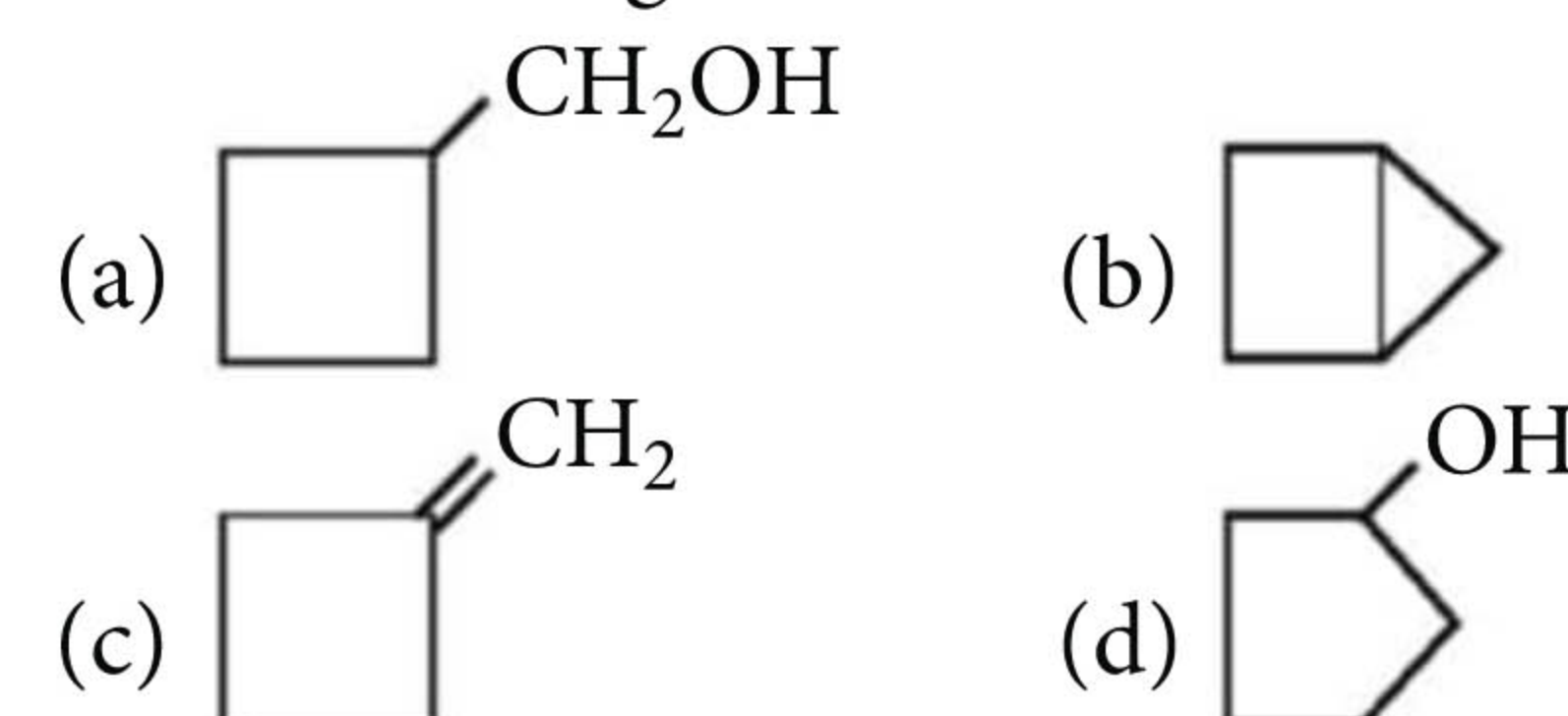
NEET / AIIMS

Only One Option Correct Type

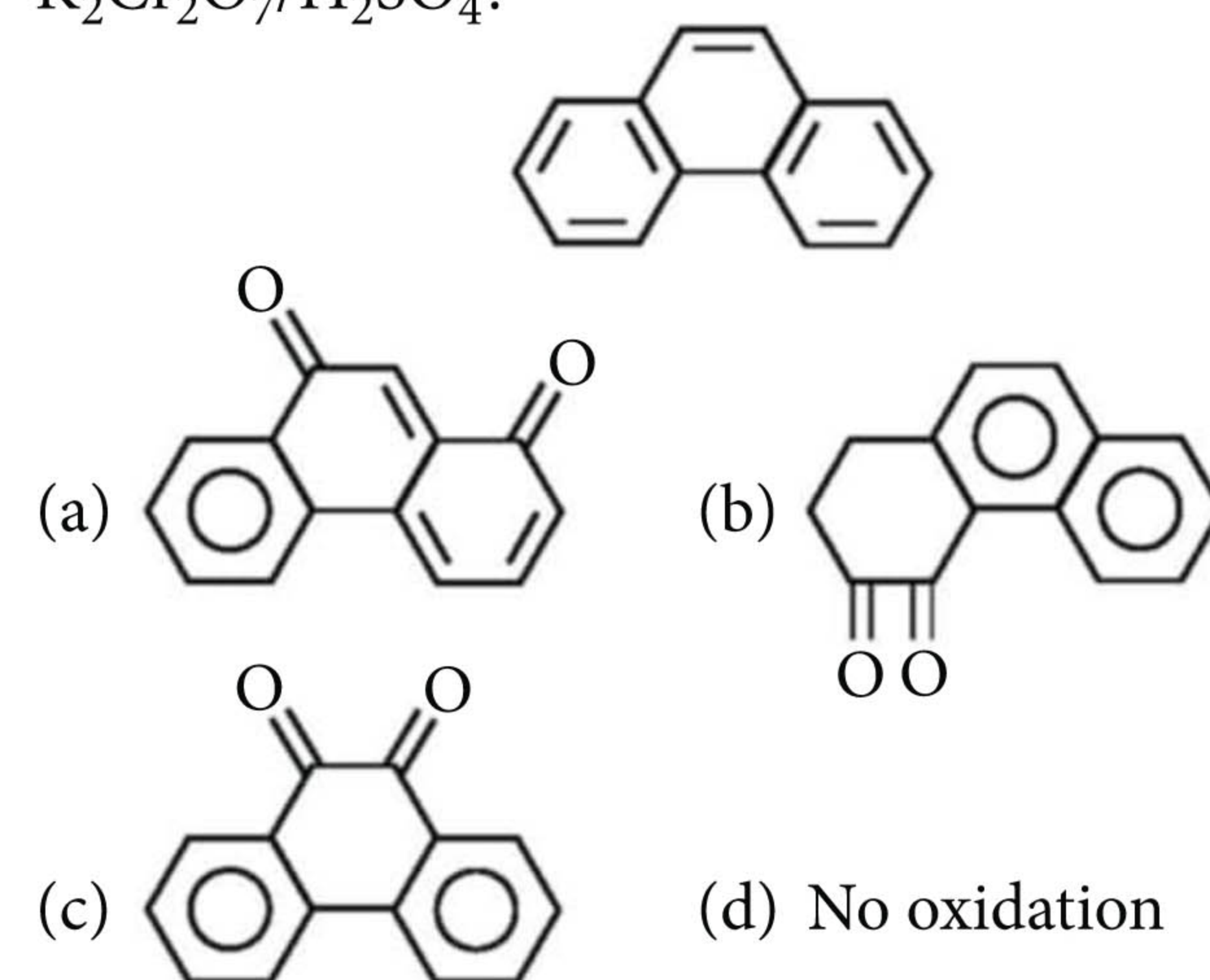
- An organic liquid has an empirical formula $C_5H_{10}O$. This liquid gives a pale yellow precipitate on warming with iodine in alkaline KI solution. The resulting salt upon acidification gives an acid which easily undergoes decarboxylation on mild heating. The structural formula of the organic liquid could be
(a) $CH_3CH_2COCH_2CH_3$
(b) $H_2C=CH-CH_2-CH(OH)-CH_3$
(c) $H_3CCH_2CH_2CH_2CHO$
(d) $CH_3CH_2CH_2OCH=CH_2$
- Which sequence of steps will be able to produce 3,3'-dinitrobiphenyl from benzene?
(a) HNO_3/H_2SO_4 , $Cl_2/FeCl_3$, Na/ether
(b) $Cl_2/FeCl_3$, HNO_3/H_2SO_4 , Na/ether
(c) $Cl_2/FeCl_3$, H_2SO_4 , Na/ether
(d) I_2/HIO_3 , $Cl_2/FeCl_3$, $C_6H_5NO_2$
- What is the name of the following compound?

(a) Ethyl 4-oxopentanoate
(b) Ethyl ester methyl ketone
(c) Ethyl 4-ketone pentanoate
(d) Ethyl 4-ketone pentyl ester
- Which of the following statements is correct?
(a) Chloral forms stable hydrate.
(b) Methanal is more reactive than ethanal towards nucleophilic addition.

- Protonated carbonyl group is more reactive towards KCN.
- All of the above.

- Treatment of cyclobutylmethylamine with nitrous acid does not give



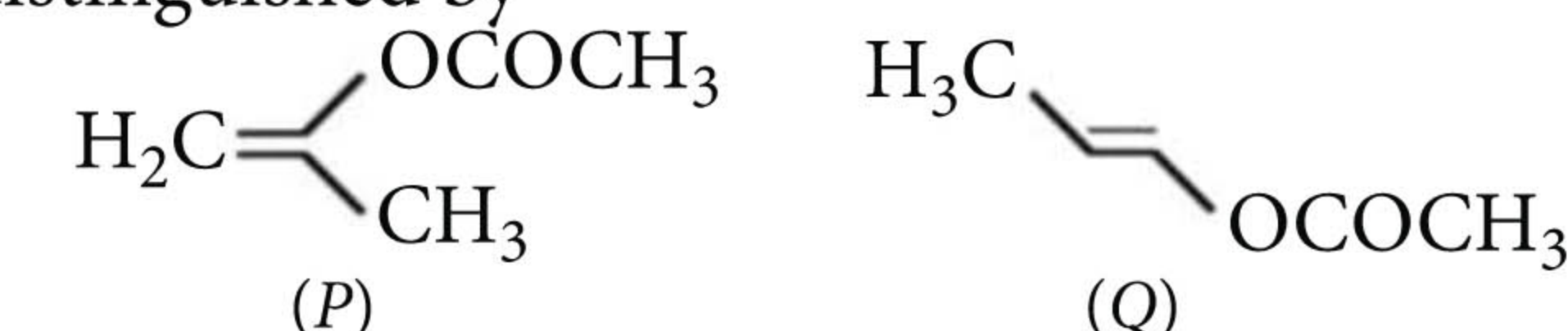
- Which of the following diketone is obtained when the following compound is strongly oxidized with $K_2Cr_2O_7/H_2SO_4$?



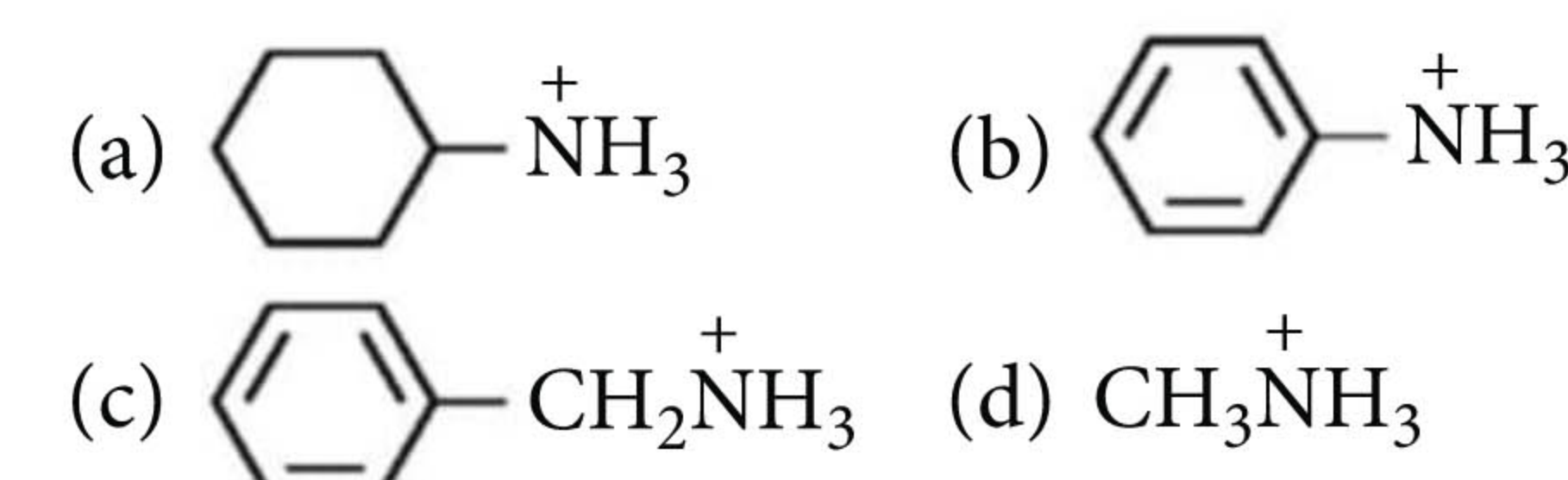
- $CH_3-C(=O)-CH_3 \xrightarrow{X_2, \bar{OH}} CHX_3 + CH_3-C(=O)-O^-$
The rate of haloform reaction is found the fastest with
(a) $X_2 = Cl_2$ (b) $X_2 = Br_2$
(c) $X_2 = I_2$
(d) All at the same rate, $r_{Cl_2} = r_{Br_2} = r_{I_2}$

- In Hofmann bromamide degradation, one of the important steps is the migration of
(a) an alkyl group without its electron pair to electron deficient N-atom
(b) an alkyl group with its electron pair to electron deficient O-atom
(c) an alkyl group with its electron pair to electron rich N-atom
(d) an alkyl group with its electron pair to electron deficient N-atom.

- The product of acid hydrolysis of P and Q can be distinguished by



- Lucas reagent
 - 2, 4-DNP test
 - Fehling's solution
 - $NaHSO_3$
- Which among the following is the strongest conjugate acid?



- The compound which is a condensation polymer can be obtained in two ways either treating 3 molecules of acetone (CH_3COCH_3) with conc. H_2SO_4 or passing propyne ($CH_3C\equiv CH$) through a red hot tube. The compound is
(a) phorone (b) mesityl oxide
(c) diacetone alcohol (d) mesitylene.

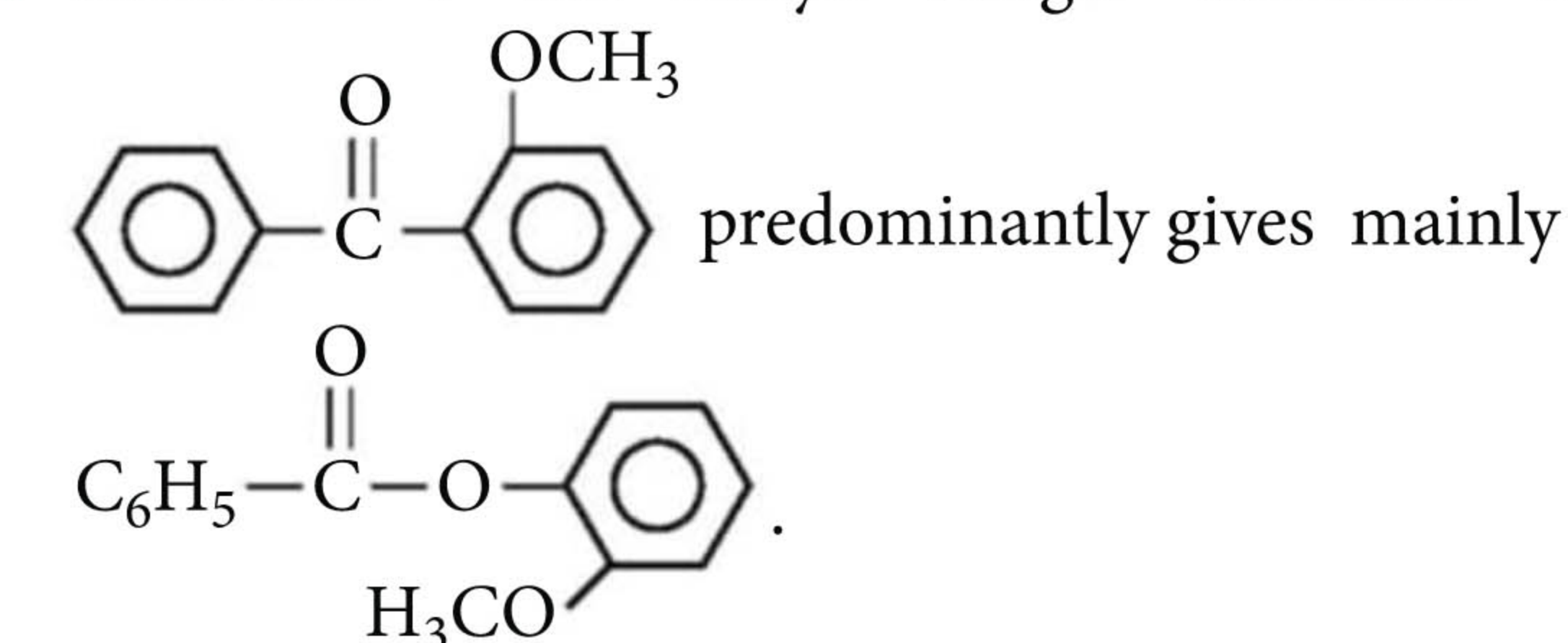
- $HC\equiv N + HCl \xrightarrow[AlCl_3]{Anhyd.} A \xrightarrow[Anhyd. AlCl_3]{C_6H_6} B \xrightarrow{H^+/H_2O} C$
In the above sequence of reactions, A, B and C respectively are
(a) $ClHC=NH$, C_6H_5Cl , C_6H_5OH
(b) $ClHC=NH$, $C_6H_5CH=NH$, C_6H_5CHO
(c) $ClHC=NH$, C_6H_5Cl , C_6H_5OH
(d) CH_2O , $C_6H_5CH_2Cl$, $C_6H_5CH_2OH$

Assertion & Reason Type

Directions : In the following questions, a statement of assertion is followed by a statement of reason. Mark the correct choice as :

- If both assertion and reason are true and reason is the correct explanation of assertion.
- If both assertion and reason are true but reason is not the correct explanation of assertion.
- If assertion is true but reason is false.
- If both assertion and reason are false.

- Assertion :** The Baeyer-Villiger oxidation of



Reason : Migratory aptitude of $-C_6H_5$ is greater than o -anisyl.

- Assertion :** Carboxylic acids contain a carbonyl group but do not give characteristic reactions of the carbonyl group.

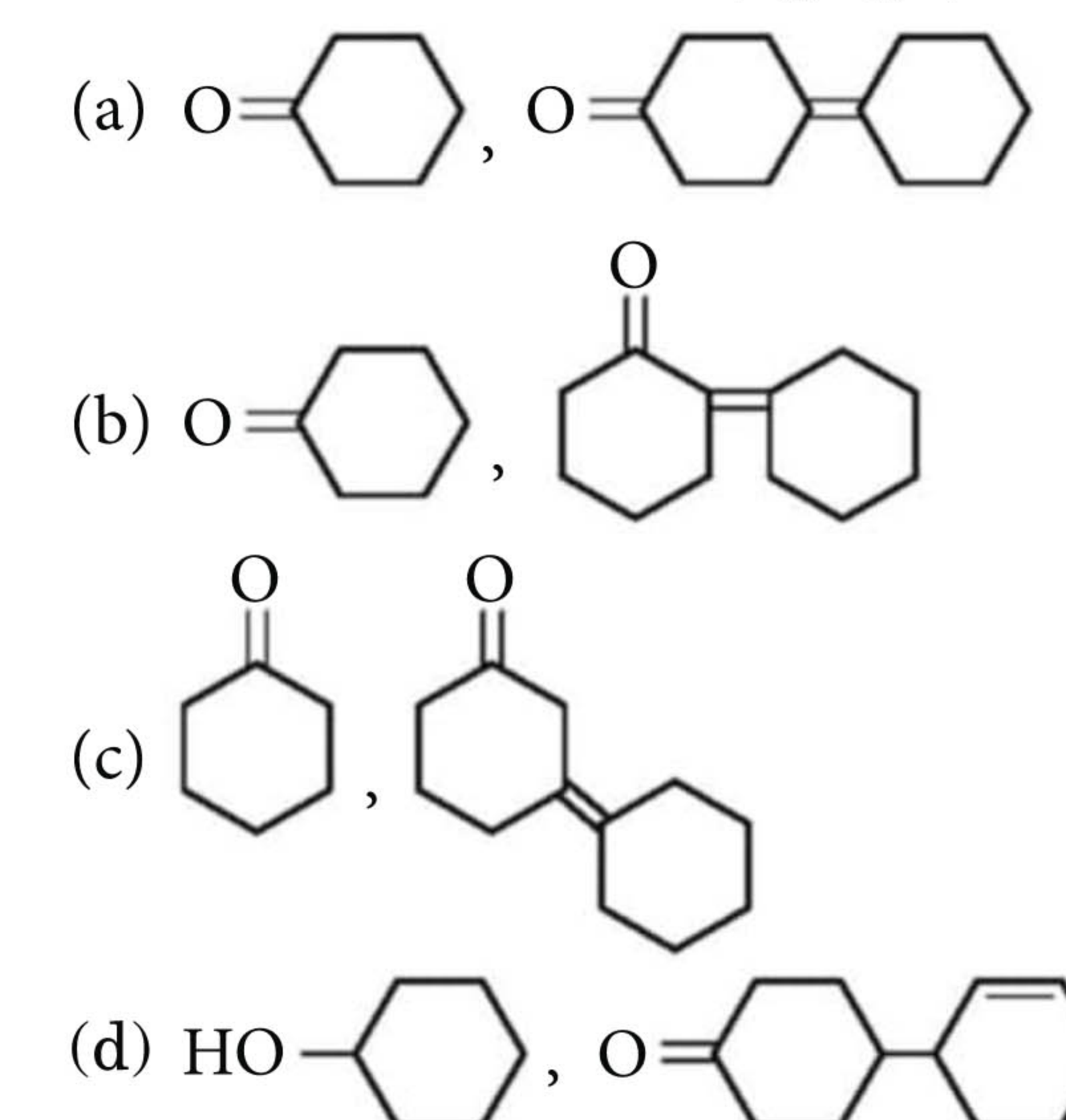
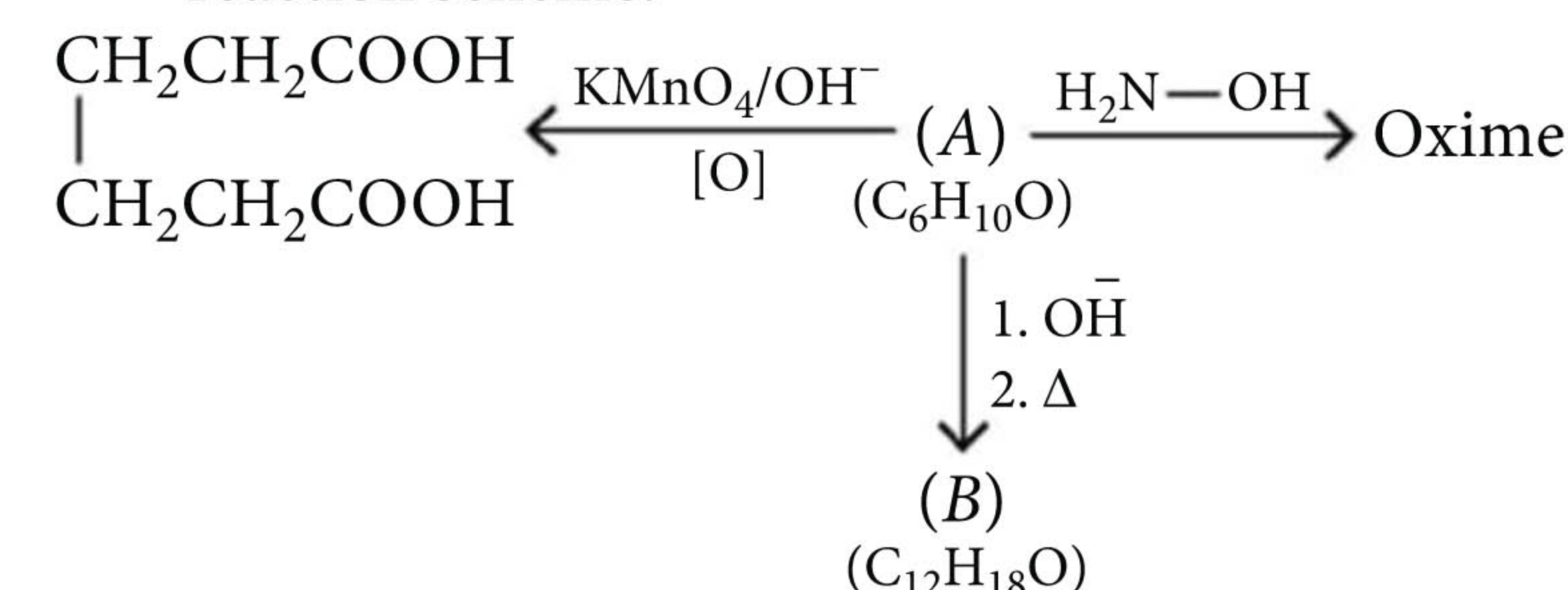
Reason : The electrophilicity of the carbonyl carbon is more in carboxylic acids than in aldehydes and ketones.

- Assertion :** m -Methoxyaniline (m -anisidine) is a stronger base than p -methoxyaniline (p -anisidine).
Reason : At m -position, methoxy group exerts both $-I$ -effect and $+R$ effect.

JEE MAIN / ADVANCED

Only One Option Correct Type

- Identify (A) and (B) based on the following reaction scheme.

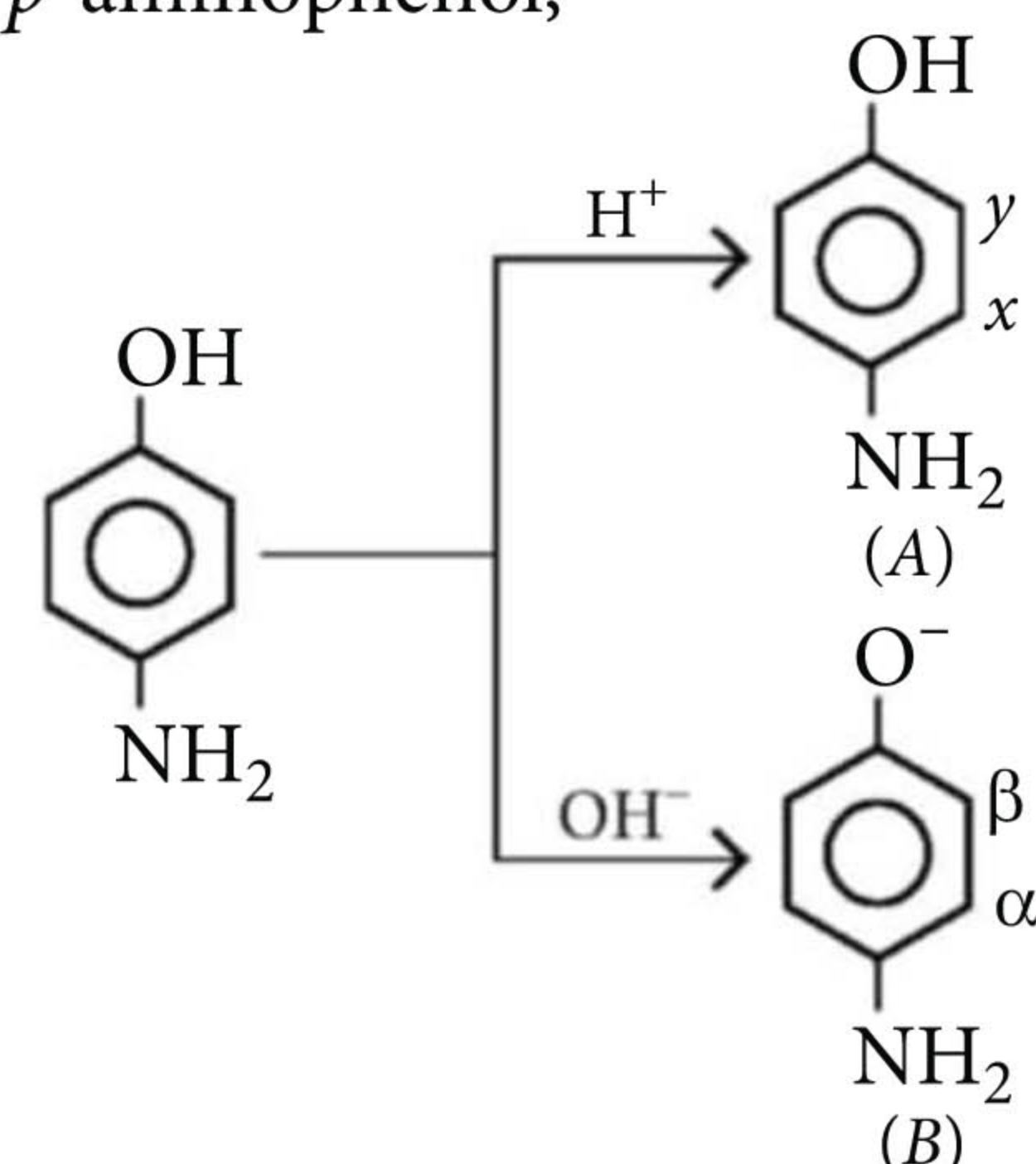


- $A \xrightarrow[EtOH, H_2O]{\Delta, CN^-} \text{Benzoin}$

The reactant (A) is obtained by dry distillation of the calcium salts of the following pairs

- (a) $C_6H_5CH_2COOH$, $HCOOH$
 (b) C_6H_5COOH , $HCOOH$
 (c) $C_6H_4(OH)COOH$, $HCOOH$
 (d) $C_6H_4(NH_2)COOH$, $HCOOH$

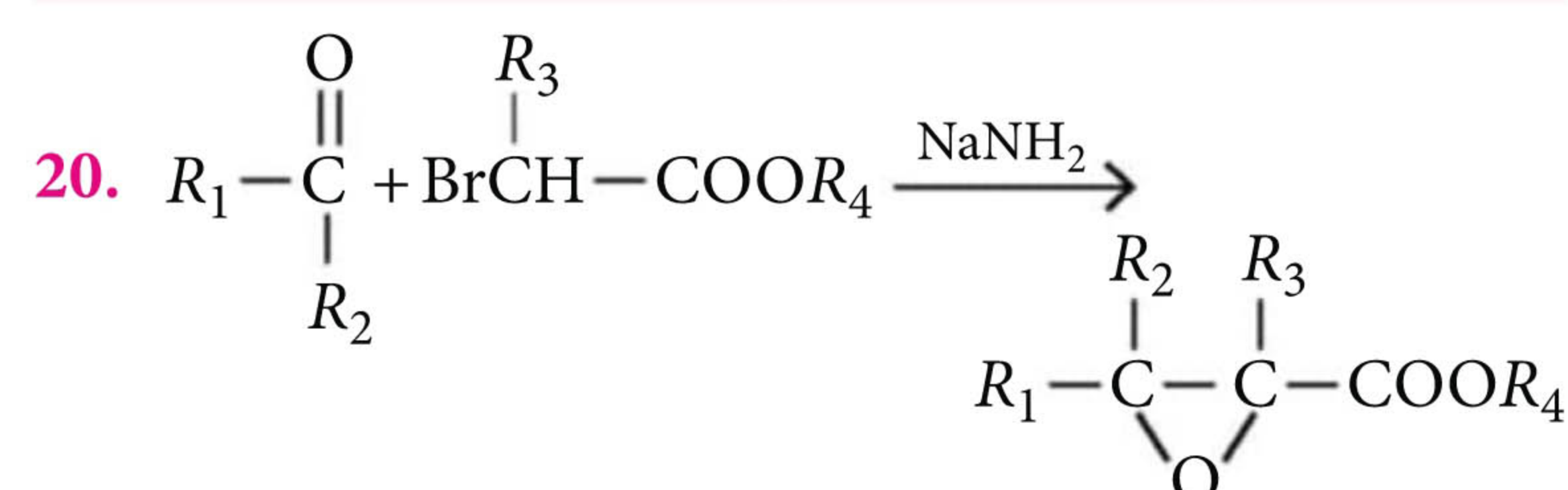
18. Consider *p*-aminophenol,



Which positions are activated for coupling reaction in acidic and basic medium respectively?

- (a) x in A and β in B (b) x in A and α in B
 (c) y in A and α in B (d) x in A and β in B
19. A compound A of formula $C_3H_6Cl_2$ on reaction with alkali can give B of formula C_3H_6O or C of formula C_3H_4 . B on oxidation gave a compound of the formula $C_3H_6O_2$. C with dilute H_2SO_4 containing Hg^{2+} ion gave D of formula C_3H_6O , which with bromine and alkali gave the sodium salt of $C_2H_4O_2$. Then A is
 (a) $CH_3CH_2CHCl_2$ (b) $CH_3CCl_2CH_3$
 (c) $CH_2ClCH_2CH_2Cl$ (d) $CH_3CHClCH_2Cl$

More than One Options Correct Type

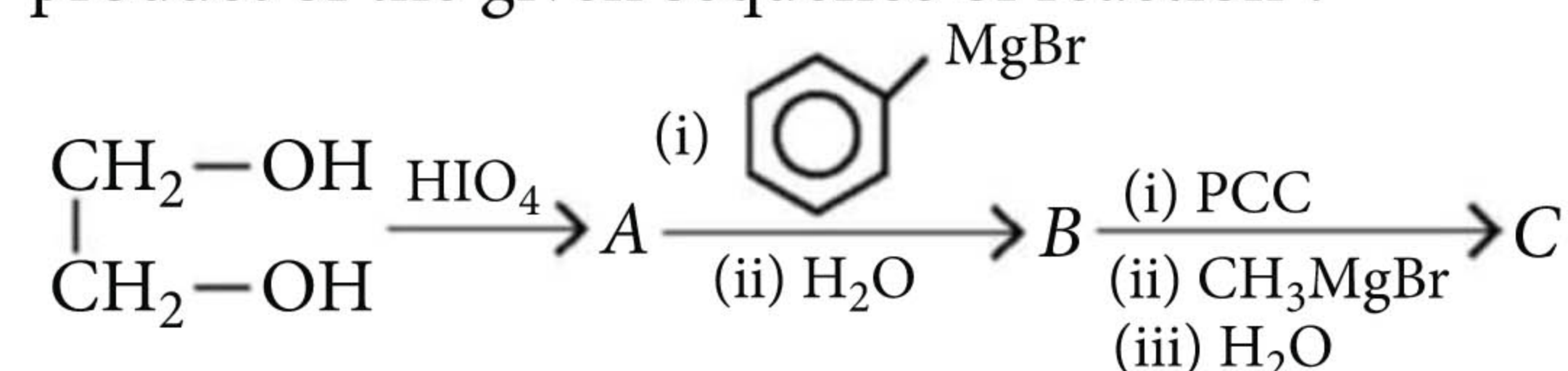


Choose the correct statement(s) regarding the above reaction.

- (a) The reaction is called Darzen's glycidic ester synthesis.
 (b) On alkaline hydrolysis of the product followed by warming with dilute acid, a new ketone forms i.e., $R_2-\overset{\overset{R_1}{\mid}}{CH}-\overset{\overset{O}{\parallel}}{C}-R_3$.
 (c) If R_4 is CMe_3 , heating of the product molecule gives a new ketone i.e., $R_2-\overset{\overset{R_1}{\mid}}{CH}-\overset{\overset{O}{\parallel}}{C}-R_3$.

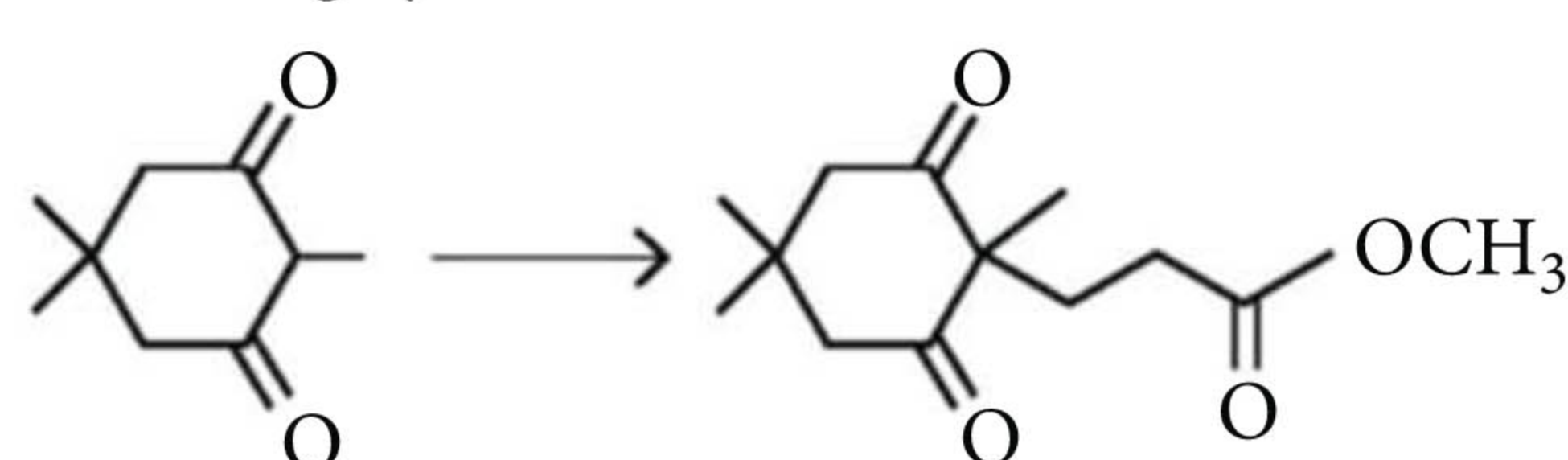
(d) The mentioned reaction may proceed more precisely if conc. OH^- is used.

21. Which of the following is correct for the final product of the given sequence of reaction?



- (a) Compound C on oxidation with $(CrO_3 + H_2SO_4)$ gives a compound which gives 2, 4- DNP test.
 (b) Compound C on reaction with $I_2 + NaOH$ gives yellow ppt.
 (c) Compound C on reaction with ceric ammonium nitrate gives red colouration.
 (d) Compound C on reaction with MnO_2 gives carboxylic acid.

22. Which of the following reagents are used in the following synthetic conversion?



- (a) *t*-BuOK (b) $H_2C=CHCOOCH_3$
 (c) H^+/H_2O (d) CH_3MgBr
23. Benzylamine may be prepared by
 (a) $C_6H_5CONH_2 \xrightarrow{LiAlH_4/ether}$
 (b) $C_6H_5CN \xrightarrow{LiAlH_4/ether}$

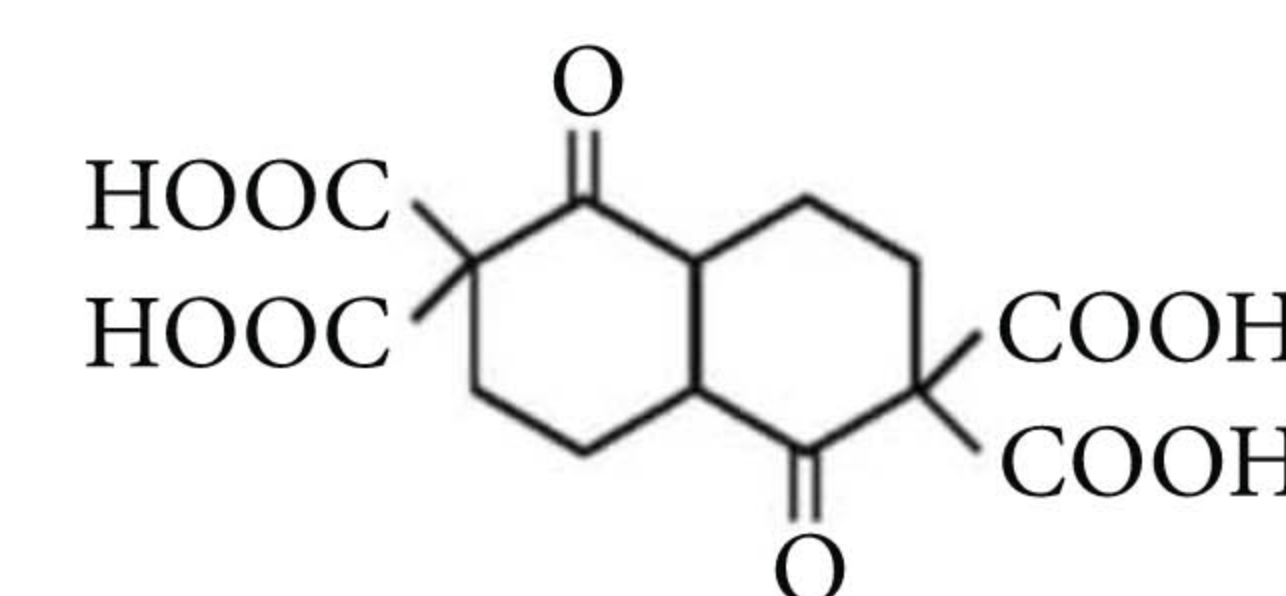
CHEMISTRY PUZZLE SOLUTION AUGUST 2019

COPPER	LITHIUM
MOLYBDENUM	DYSPROSIUM
VANADIUM	THORIUM
AMERICIUM	MERCURY
RADIUM	OSMIUM
SODIUM	IODINE
SILICON	GADOLINIUM
CURIUM	TIN
ZIRCONIUM	BROMINE
POTASSIUM	TITANIUM
NEPTUNIUM	CADMIUM
NEON	FLUORINE
HOLMIUM	LUTETIUM
INDIUM	LAWRENCIUM

- (c) Phthalimide $\xrightarrow[(iii) aq. NaOH, \Delta]{(i) KOH, (ii) C_6H_5CH_2Br}$
 (d) $C_6H_5CH_2CONH_2 \xrightarrow{NaOBr}$

Numerical Value Type

24. $CH_3-CH=CH-\overset{\overset{H}{\mid}}{C}=O$ (excess) $\xrightarrow[\Delta]{LDA}$
 The DBE of the product in the above reaction is
25. How many of the following amines do not evolve N_2 on treatment with $NaNO_2/HCl$?
 Aniline, *N*-methylaniline, *N,N*-dimethylaniline, diethylamine, ethylamine, *p*-toluidine, benzylmethylamine, *o*-anisidine, *m*-chloroaniline
26. How many moles of CO_2 will be released when the following compound is heated?



Matrix Match Type

Answer the following questions (27 and 28) by appropriately matching the columns based on the information given in the passage:

The value of K_b describes the relative strength of the bases. Strong bases have higher values of K_b while weak bases have low values.

A more convenient method of expressing the basic strength of amines is in terms of pK_b values ($pK_b = -\log K_b$). Smaller the value of pK_b , more is the basic strength of amine.

Column-I (Amine)	Column-II (pK_b value)
A. CH_3NH_2	P. 4.22
B. $(CH_3)_2NH$	Q. 9.38
C. $(CH_3)_3N$	R. 3.38
D. $C_6H_5NH_2$	S. 3.27

27. Which of the following has the correct combination considering column-I and column-II?

- (a) $A \rightarrow R$ (b) $B \rightarrow P$
 (c) $C \rightarrow Q$ (d) $D \rightarrow S$

28. Which of the following has the correct combination considering column-I and column-II?

- (a) $A \rightarrow S$ (b) $B \rightarrow Q$
 (c) $C \rightarrow P$ (d) $D \rightarrow S$

Answer the following questions (29 and 30) by appropriately matching the columns based on the information given in the passage :

Aldehydes and ketones on reduction give 1° and 2° alcohols respectively. Reduction of carbonyl compounds carried out either catalytically with H_2 or by other reducing agents like metal amalgam and alcohols or simple hydrocarbons are formed.

Column-I	Column-II	Column-III
A. $CH_3CHO \xrightarrow{Zn/Hg, HCl}$	P. $(CH_3)_2CH-OH$	W. Clemmensen reduction
B. $CH_3COCH_3 \xrightarrow{[H]}$	Q. $(CH_3)_2C(OH)-C(OH)(CH_3)_2$	X. $LiAlH_4$ reduction
C. $CH_3COCH_3 \xrightarrow{NH_2NH_2, OH^-}$	R. $CH_3CH_2CH_3$	Y. Pinacol reduction
D. $CH_3COCH_3 \xrightarrow[Mg/Hg]{H_2O}$	S. CH_3CH_3	Z. Wolff-Kishner reduction

29. Which of the following has the correct combination considering column-I and column-II?

- (a) $A \rightarrow S, W$ (b) $B \rightarrow P, W$
 (c) $C \rightarrow Q, Z$ (d) $D \rightarrow R, X$

30. Which of the following has the correct combination considering column-I and column-II?

- (a) $A \rightarrow P, W$ (b) $B \rightarrow Q, X$
 (c) $C \rightarrow R, Z$ (d) $D \rightarrow P, Y$

Keys are published in this issue. Search now! ☺

SELF CHECK

No. of questions attempted
 No. of questions correct
 Marks scored in percentage

Check your score! If your score is

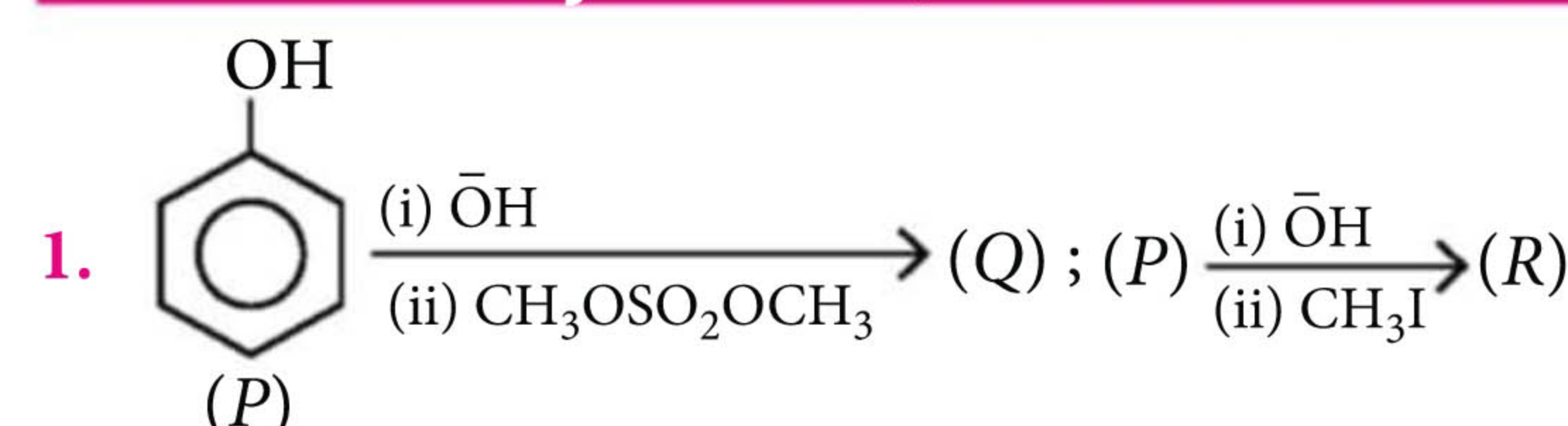
> 90%	EXCELLENT WORK !	You are well prepared to take the challenge of final exam.
90-75%	GOOD WORK !	You can score good in the final exam.
74-60%	SATISFACTORY !	You need to score more next time.
< 60%	NOT SATISFACTORY!	Revise thoroughly and strengthen your concepts.

CHEMISTRY MUSING

PROBLEM SET 74

Chemistry Musing was started from August '13 issue of Chemistry Today. The aim of Chemistry Musing is to augment the chances of bright students preparing for JEE (Main and Advanced) / NEET / AIIMS / JIPMER with additional study material. In every issue of Chemistry Today, 10 challenging problems are proposed in various topics of JEE (Main and Advanced) / NEET. The detailed solutions of these problems will be published in next issue of Chemistry Today. The readers who have solved five or more problems may send their solutions. The names of those who send atleast five correct solutions will be published in the next issue. We hope that our readers will enrich their problem solving skills through "Chemistry Musing" and stand in better stead while facing the competitive exams.

JEE MAIN/NEET



The products (Q) and (R), respectively, are

(a) PhOCH_3 , PhOCH_3

(b) $\text{Ph}-\text{O}-\text{S}(=\text{O})_2-\text{OCH}_3$, PhOCH_3

(c) $\text{Ph}-\text{O}-\text{S}(=\text{O})_2-\text{CH}_3$, PhCOCH_3

(d) PhOSO_3H , PhOCH_3

2. Which of the following statements is correct for the $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]\text{SO}_4$ complex?

(a) The EAN value of Fe in this complex depends on the charge of NO ligand.

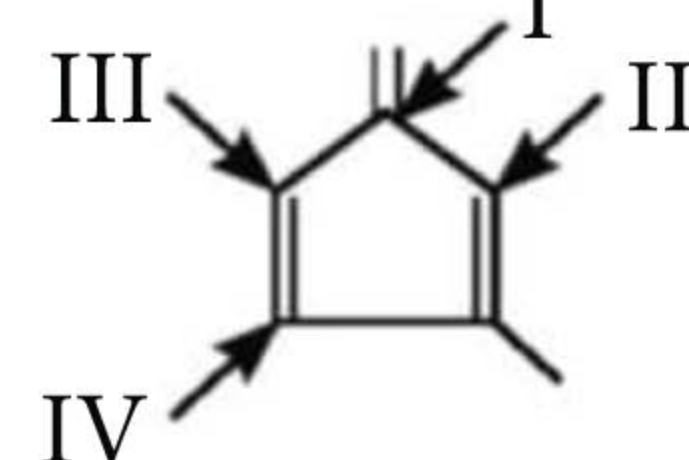
(b) The EAN value of Fe in this complex does not depend on the charge of NO ligand.

(c) The hybridisation of the central atom is d^2sp^3 .

(d) It is paramagnetic with $\mu = 1.73$ B.M.

3. Which is the least likely protonation site in the conjugated alkene shown below?

- (a) I
(b) II
(c) III
(d) IV



4. The equilibrium constants K_{p1} and K_{p2} for the reactions $X \rightleftharpoons 2Y$ and $Z \rightleftharpoons P + Q$ respectively are in the ratio of 1 : 9. If the degree of dissociation of X and Z be equal, the ratio of the total pressure at these equilibria is

- (a) 1 : 36 (b) 1 : 1 (c) 1 : 3 (d) 1 : 9

5. Which of the following statements is correct?

(a) The Ruff procedure lengthens an aldose chain and gives a single product.

(b) The Ruff procedure shortens an aldose chain and gives two epimers.

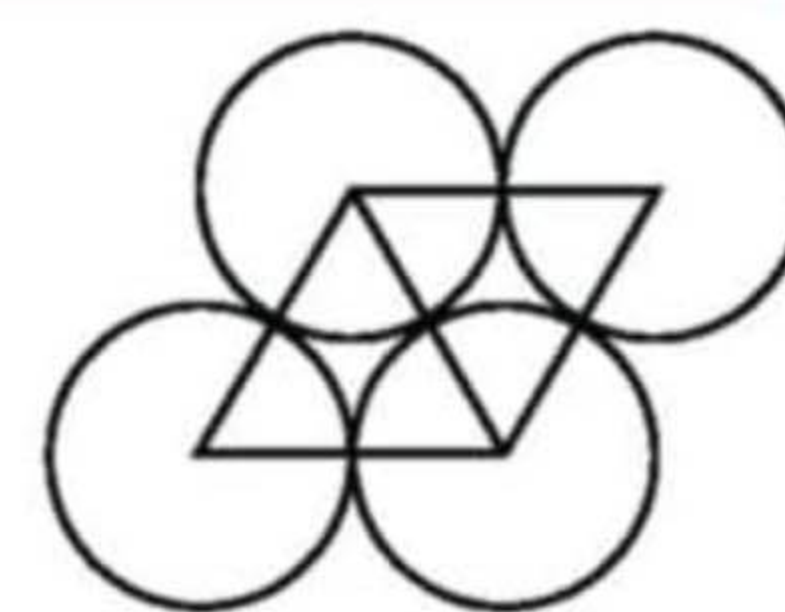
(c) The Kiliani-Fischer procedure shortens an aldose chain and gives a single product.

(d) The Kiliani-Fischer procedure lengthens an aldose chain and gives two epimers.

JEE ADVANCED

6. Structure of unit cell is shown in the given figure. Fraction of the unit cell is

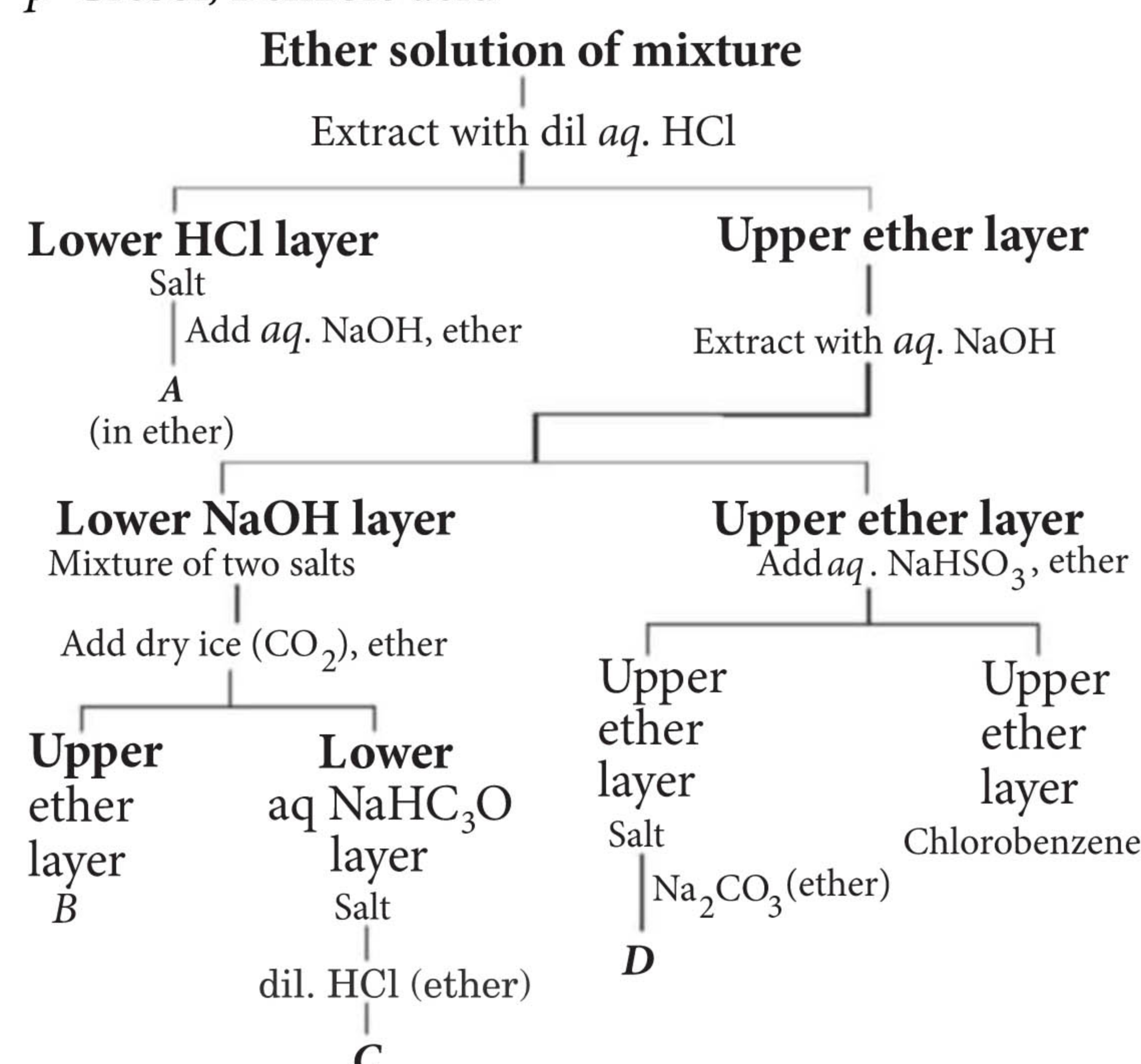
- (a) 0.521 (b) 0.907
(c) 0.093 (d) 0.745



COMPREHENSION

Analyse the following flow sheet to show the separation and recovery in almost quantitative yield of a mixture of the water insoluble compounds :

Benzaldehyde, *N,N*-dimethylaniline, Chlorobenzene, *p*-Cresol, Benzoic acid



7. The compound 'C' is
(a) *N,N*-dimethylaniline
(b) benzoic acid
(c) *p*-cresol (d) benzaldehyde.
8. The compound 'D' is
(a) *N,N*-dimethylaniline
(b) benzoic acid
(c) *p*-cresol (d) benzaldehyde.

NUMERICAL VALUE

9. One litre of CO_2 gas is passed over hot coke. The final volume of gas is 1.6 L. The amount of CO_2 left

unreacted is (If the volume measurement are made at the same temperature and pressure)

10. For the reversible reaction in equilibrium $A \xrightleftharpoons[k_2]{k_1} B$
The values of k_1 and k_2 are $2 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$ and $3 \times 10^{-3} \text{ s}^{-1}$ respectively. If we add 0.5 moles of B in the equilibrium mixture, initially containing 2 moles of A. Calculate the time taken for concentration of B to become equal to 3/4 of the concentration of A at initial equilibrium. The volume of mixture is 1 L and remains constant.

Scientist who Made Us Proud

Sir Shanti Swarup Bhatnagar was an Indian colloid chemist, academic and scientific administrator. The first director-general of the Council of Scientific and Industrial Research (CSIR), he is revered as the "father of research laboratories" in India. He was also the first Chairman of the University Grants Commission (India) (UGC).

In 1958, to honour his name and legacy, the Indian Council of Scientific and Industrial Research (CSIR) instituted the Shanti Swarup Bhatnagar Prize for Science and Technology for scientists who have made significant contributions in various branches of science.



Shanti Swarup Bhatnagar
(21 February, 1894 – 1 January, 1955)

Early Life and Education

Bhatnagar was born in the Bhera, Punjab region of British India. His father, Parmeshwari Sahai Bhatnagar, died when he was eight months old, and he spent his childhood in the house of his maternal grandfather, an engineer, who helped him develop a liking for science and engineering. He enjoyed building mechanical toys, electronic batteries, and string telephones. From his maternal family he also inherited a gift of poetry. He completed his elementary education from the Dayanand Anglo-Vedic High School, Sikandrabad (Bulandshahr). In 1911 he joined the newly established Dayal Singh College, Lahore where he became an active member of the Saraswati Stage Society and earned a good reputation as an actor. Bhatnagar passed the Intermediate Examination of the Punjab University in 1913 in first class and joined the Forman Christian College, where he obtained a BSc in physics in 1916, and a MSc in chemistry in 1919.

He earned his Doctorate in Science in 1921. He was supported by the British Department of Scientific and Industrial Research with a fellowship.

He joined the newly established Banaras Hindu University (BHU) as a professor of chemistry.

Research and Contributions

- His research interests included emulsions, colloids, and industrial chemistry but his fundamental contributions were in the field of magneto-chemistry, the use of magnetism for the study of chemical reactions.

- In 1928 he and K.N. Mathur jointly developed the Bhatnagar-Mathur Magnetic Interference Balance, which was one of the most sensitive instruments at the time for measuring magnetic properties.
- His major innovation was an improvement of the procedure for drilling crude oil.
- Bhatnagar persuaded the government to set up an Industrial Research Utilisation Committee (IRUC) in early 1941 for further investment into industrial research. Mudaliar also won the demand for an establishment of Industrial Research Fund, at the Central Assembly in Delhi at its session on 14 November 1941. These finally led to the constitution of the Council of Scientific and Industrial Research (CSIR) as an autonomous body. In 1943 the governing body approved the proposal mooted by Bhatnagar to establish five national laboratories — the National Chemical Laboratory, the National Physical Laboratory, the Fuel Research Station, and the Glass and Ceramics Research Institute. This was the beginning of scientific laboratories in India.

Awards and Honours

- Bhatnagar was elected one of the first Fellows of the Indian Academy of Sciences (FASc) in 1934; he was appointed a Foundation Fellow of the National Institute of Sciences of India (FNI; now the Indian National Science Academy) the following year.
- For his contributions to pure and applied chemistry, Bhatnagar was appointed an Officer of the Order of the British Empire (OBE) in 1936.
- The British government knighted him in the 1941 New Year Honours List for his contributions to the advancement of science. Bhatnagar was appointed a Fellow of the Institute of Physics (FInstP) in 1942, and was also appointed a Fellow of the Royal Institute of Chemistry (FRIC) that year.
- In 1943 the Society of Chemical Industry, London, elected him as Honorary Member and later as Vice President. Bhatnagar was elected a Fellow of the Royal Society (FRS) in 1943.
- In independent India, he was the President of the Indian Chemical Society, National Institute of Sciences of India and the Indian National Science Congress. He was awarded Padma Bhushan by the government of India in 1954.
- A prestigious Indian science award, Shanti Swarup Bhatnagar Prize for Science and Technology was created in his honour.



CONCEPT BOOSTER

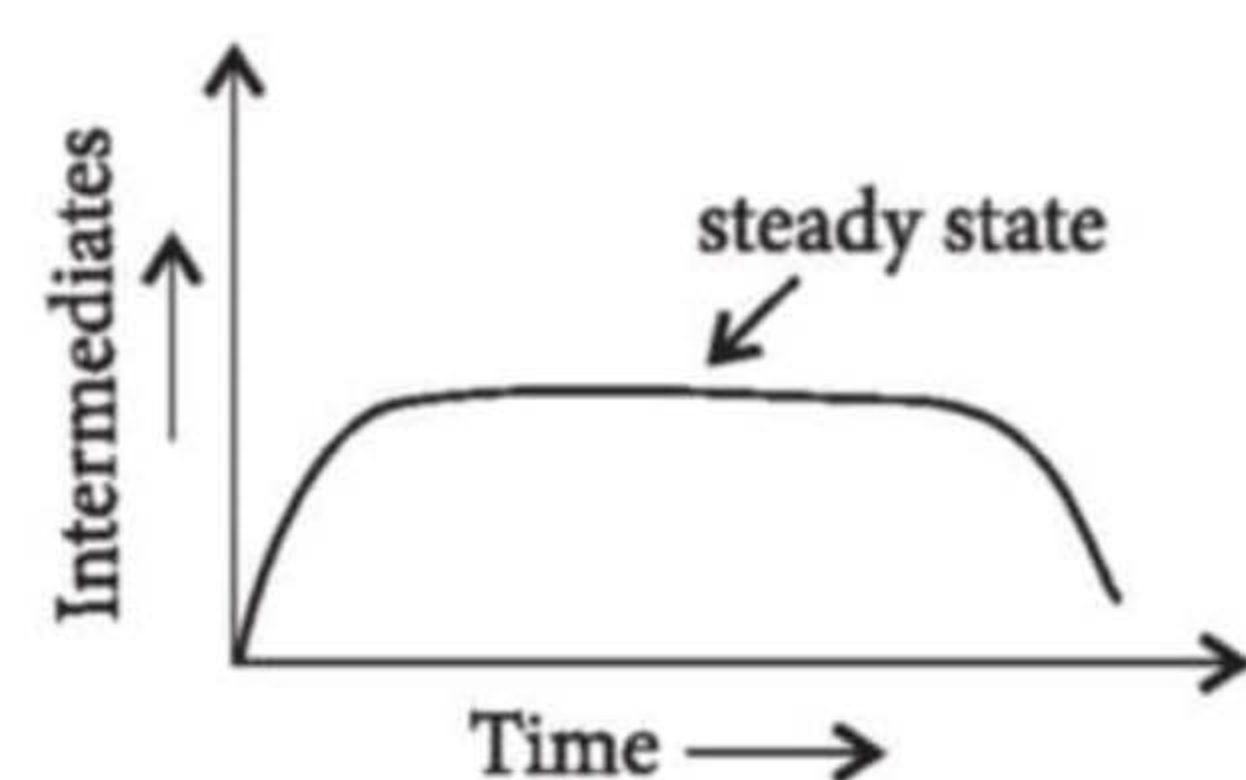
CHEERS!! My students, hope you all are fine. Hope life is a sunshine. To keep you all on track so that you can shine like a blazing star, CHEMISTRY TODAY TEAM including me is always beside you all. This article reflects that. A topic which students often ignore is discussed in a lucid manner. Try to get into the depth of the subject, try to touch a tough topic gently. I have given such a topic this month. This is STEADY STATE APPROXIMATION (SSA). It is quite an important topic for competitive examinations. Hope you all will like it.

*Arunava Sarkar

Steady State Approximation (SSA)

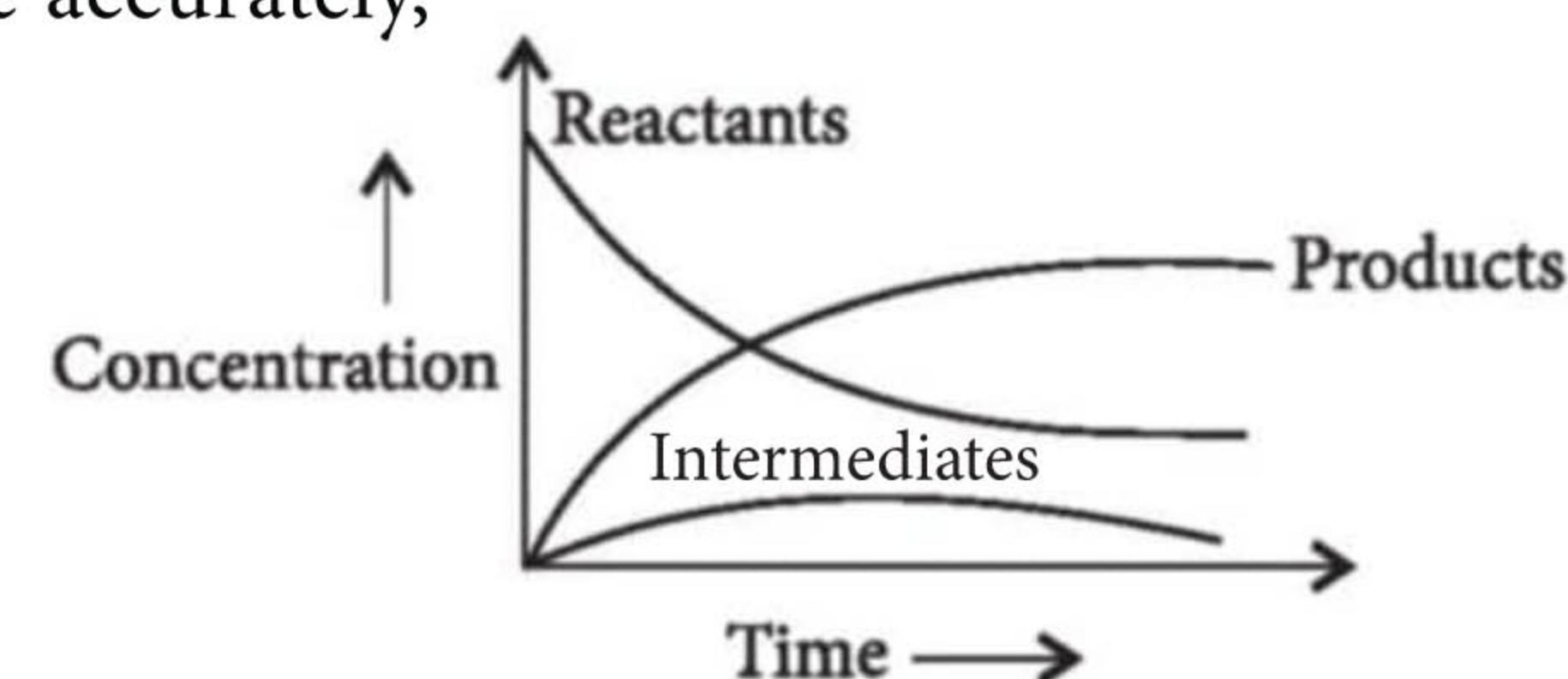
Kinetics of a reaction becomes very complex if it involves more than one step. In that case an alternative approach is used which is known as Steady State Approximation (SSA).

Basic assumption of SSA is that after an initial induction of an interval during which the concentration of involved intermediates rises from zero and change of concentration of all reaction intermediates are negligible. Actually, in most of the cases, reaction start with reactants and rate of production of intermediate is large in comparison to consumption but after some time rate of consumption of intermediate becomes equal to its rate of production. This is known as steady state of reaction. Almost at the end, when reaction gets completed, rate of consumption will become more than rate of production. But, for most of the reaction, steady state is observed.



At steady state, $\frac{d[\text{intermediate}]}{dt} = 0$

More accurately,



There are three types of reactions where SSA is applied.

- Type-1** : First step is slow, second step is rapid.

Example : $2\text{O}_3 \xrightarrow{k} 3\text{O}_2$ (complete reaction)

Step-1 : $\text{O}_3 \xrightarrow{k_1} \text{O}_2 + \text{O}$ (slow)

Step-2 : $\text{O} + \text{O}_3 \xrightarrow{k_2} 2\text{O}_2$ (fast)

For the first reaction,

$$-\frac{d[\text{O}_3]}{dt} = +\frac{d[\text{O}_2]}{dt} = +\frac{d[\text{O}]}{dt} = k_1[\text{O}_3] \quad \dots(1)$$

Here, rate = $k_1[\text{O}_3]$

Check one thing carefully. Here, you've already been given which is slow step. But, the concept of SSA is applicable only where the slow step will not be mentioned.

Now, for the second reaction,

$\text{O} + \text{O}_3 \xrightarrow{k_2} 2\text{O}_2$

$$\therefore -\frac{d[\text{O}]}{dt} = -\frac{d[\text{O}_3]}{dt} = +\frac{1}{2} \frac{d[\text{O}_2]}{dt} = k_2[\text{O}][\text{O}_3]$$

$$\therefore \frac{d[\text{O}_2]}{dt} = 2k_2[\text{O}][\text{O}_3] \quad \dots(2)$$

From eqn. (1) and (2)

$$\frac{d[\text{O}_2]}{dt} = k_1[\text{O}_3] + 2k_2[\text{O}][\text{O}_3] \quad \dots(3)$$

$$\text{Similarly, } \frac{d[\text{O}]}{dt} = k_1[\text{O}_3] - k_2[\text{O}][\text{O}_3] = 0$$

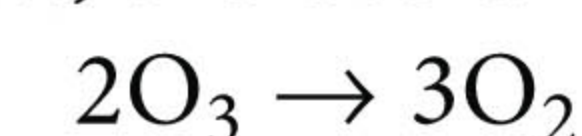
(Applying SSA)

$$\therefore [\text{O}] = \frac{k_1}{k_2}$$

Now putting this value in eq. (3), we have

$$\frac{d[\text{O}_2]}{dt} = k_1[\text{O}_3] + 2k_2 \cdot \frac{k_1}{k_2} [\text{O}_3] = 3k_1[\text{O}_3]$$

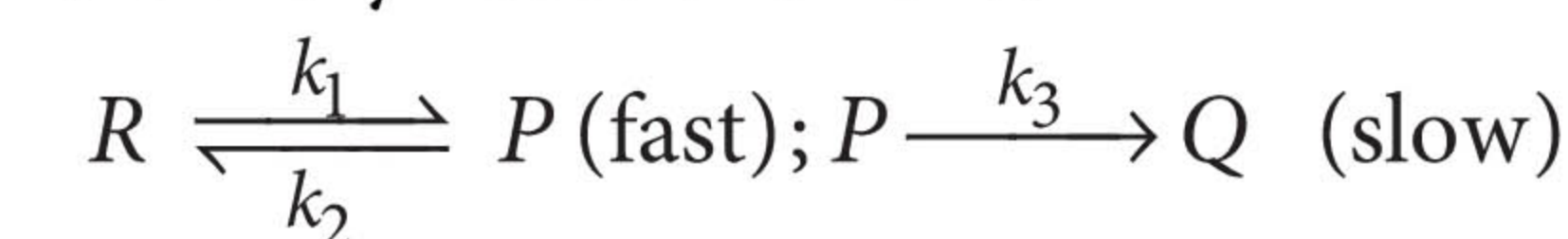
Now, the overall reaction was



$$\therefore \text{Rate} = -\frac{1}{2} \frac{d[\text{O}_3]}{dt} = \frac{1}{3} \frac{d[\text{O}_2]}{dt} = \frac{1}{3} \cdot 3k_1[\text{O}_3] = k_1[\text{O}_3]$$

- Type-2** : First step is fast equilibrium, second step is slow step.

For arbitrary reactions here,



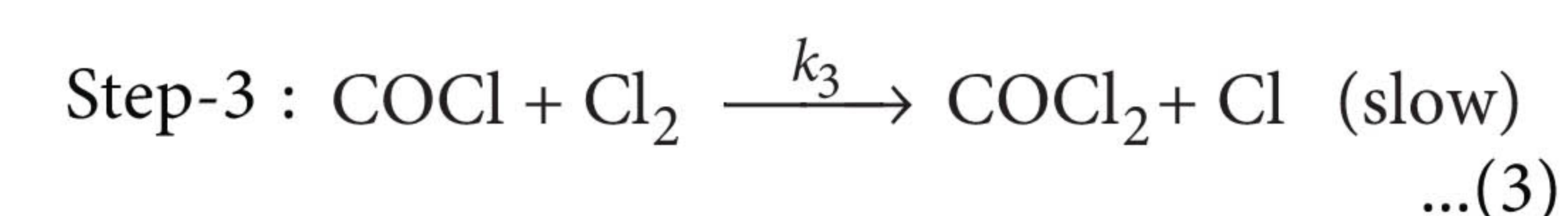
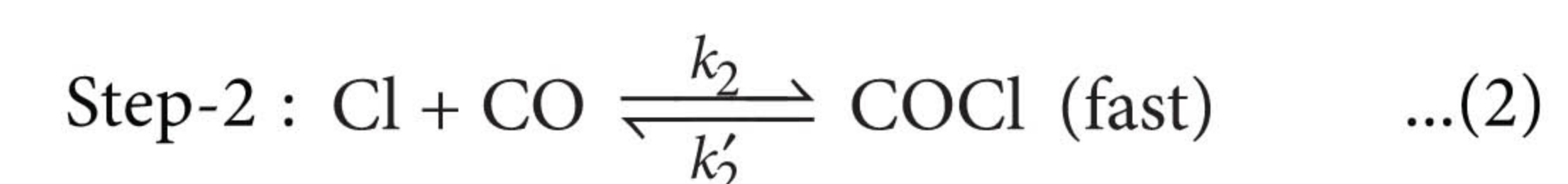
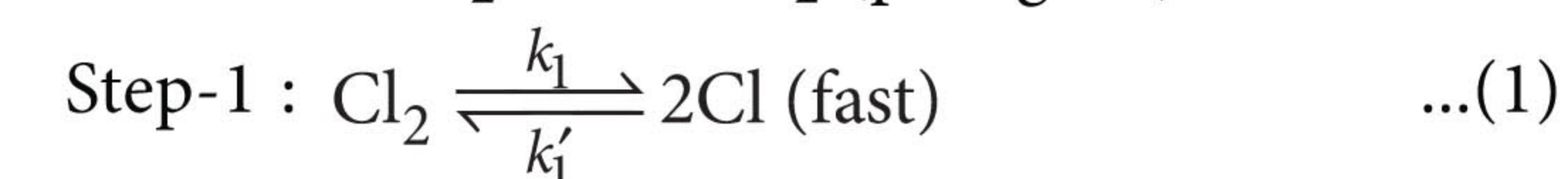
$$\text{Now, } \frac{d[Q]}{dt} = k_3[P] \text{ and}$$

$$\frac{[P]}{[R]} = \frac{k_1}{k_2} \Rightarrow [P] = \frac{k_1}{k_2}[R]$$

$$\therefore \frac{d[Q]}{dt} = k_3 \cdot \frac{k_1}{k_2} [R]$$

- Type-3** : Here more than two elementary steps are involved with only one slow step.

The best example is



Now from eq., (3)

$$\frac{d[\text{COCl}_2]}{dt} = k_3[\text{COCl}][\text{Cl}_2] \quad \dots(4)$$

$$(2) \Rightarrow \frac{k_2}{k_2'} = \frac{[\text{COCl}]}{[\text{Cl}][\text{CO}]} \Rightarrow [\text{COCl}] = \frac{k_2}{k_2'}[\text{Cl}][\text{CO}]$$

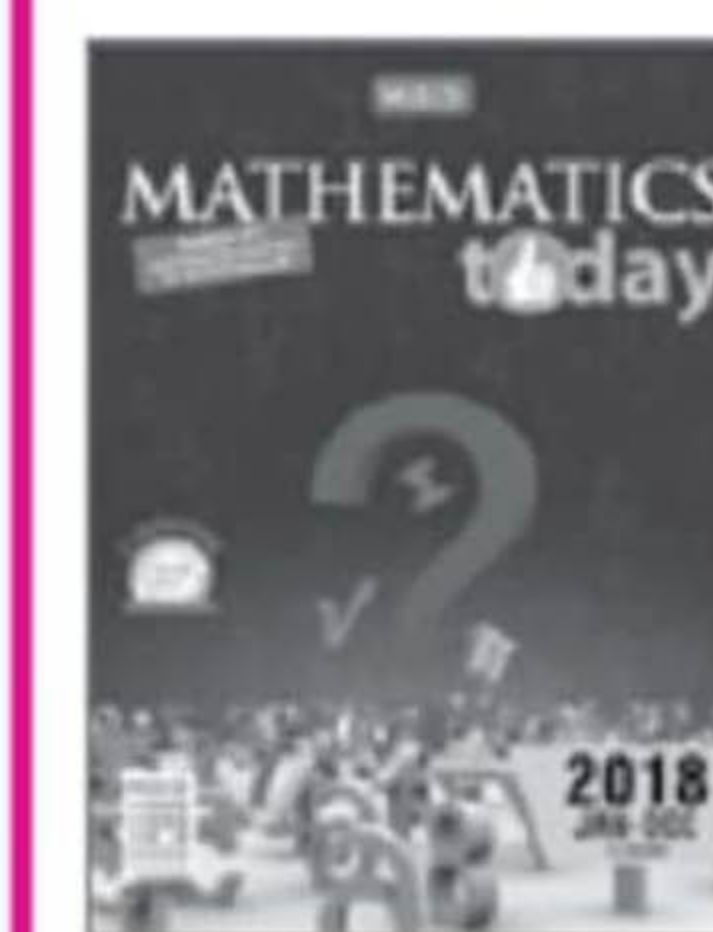
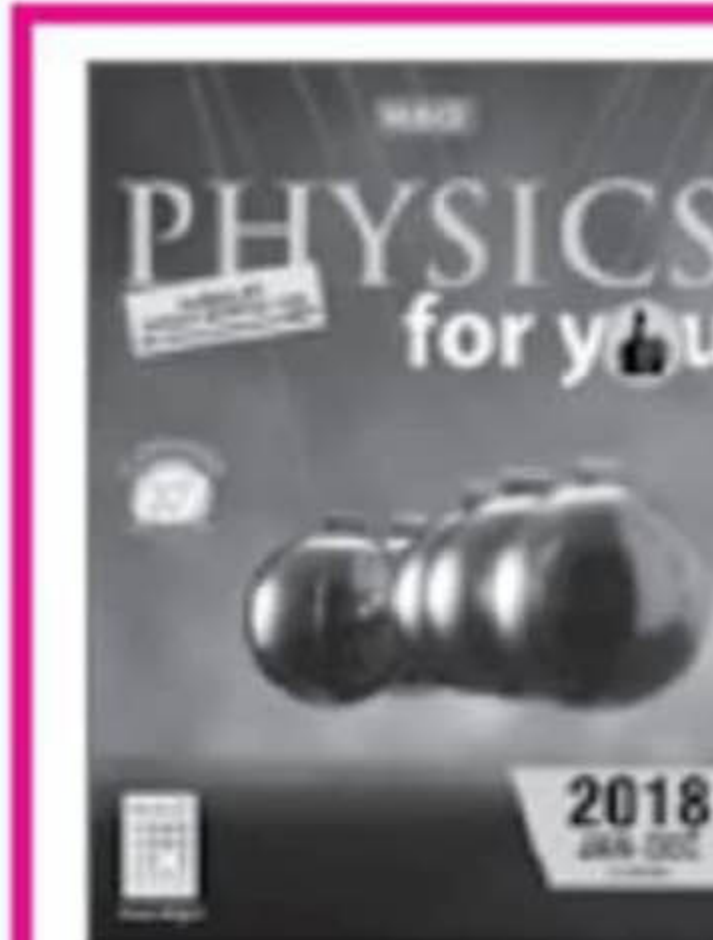
$$(1) \Rightarrow \frac{k_1}{k_1'} = \frac{[\text{Cl}]^2}{[\text{Cl}_2]} \Rightarrow [\text{Cl}] = \sqrt{\frac{k_1}{k_1'}} [\text{Cl}_2]^{1/2}$$

$$\therefore [\text{COCl}] = \frac{k_2}{k_2'} \cdot [\text{Cl}] \cdot [\text{CO}]$$

$$= \frac{k_2}{k_2'} \cdot \left(\frac{k_1}{k_1'} \right)^{1/2} [\text{Cl}_2]^{1/2} [\text{CO}]$$

$$\therefore \text{Rate} = \frac{d[\text{COCl}_2]}{dt} = \frac{k_3 \cdot k_2}{k_2'} \cdot \left(\frac{k_1}{k_1'} \right)^{1/2} [\text{Cl}_2]^{3/2} [\text{CO}]$$

AVAILABLE BOUND VOLUMES



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Readers' CAFE

Dear Readers,

We have been receiving a lot of queries from students and their parents, so we decided to ease you out by introducing a new column to guide you through your worries, concerns and questions related to your studies and beyond. Readers can send their queries (concerns beyond specific subjects, career guidance, tips for better performance, etc.) by post or by email at editor@mtg.in. The solutions to your queries given by MTG experts will definitely ease your anxiety and provide you a clear vision and a right direction to achieve your goals. Best and most relevant questions will be chosen and published with the sender's name.

V What study plan should I follow to get 95% in class 12th CBSE board exams? (Anurag Kashyap, New Delhi)

First of all try to build strong foundation from the start of the session. Make your concepts strong by thoroughly revising the topics right after teacher taught you in the class.

Also focus on question solving strategy to practice more and more. Refer to authentic self-guides/ question banks to prepare thoroughly.

MTG Excel series for class-12 Chemistry, Physics, Biology and Mathematics will help you as it contains theory, solved questions of NCERT, previous years' papers and important questions chapterwise-topicwise as well. You can also refer to MTG NCERT Textbook & Exemplar Problems Solutions and MTG CBSE Champion series (last 10 years' question bank topicwise).

V Which chapters are most important and what is the weightage of chapters of class 12th for CBSE Board examination? (Ria Maheshwari, Rajasthan)

First of all, go through the CBSE syllabus which provides the weightage of the three sections : 23 marks for Physical Chemistry, 19 marks for Inorganic Chemistry, 28 marks for Organic Chemistry.

- **2019 & 2018 CBSE Board Paper Analysis shows that**
 - 5 Marks Questions were asked from Electrochemistry, Chemical Kinetics, The *p*-Block Elements and Amines.
 - 2 Marks and 3 Marks Questions were asked heavily from Solutions, Chemical Kinetics, Surface Chemistry, General Principles & Processes of isolation of elements, The *d*- and *f*-Block Elements, Coordination Compounds, Haloalkanes & Haloarenes, Aldehydes, Ketones and Carboxylic Acids.

- **2017 CBSE Board Paper (Delhi) Analysis shows that**

- 5 Marks Questions were asked from The *d*- and *f*-Block Elements, Alcohols, Phenols and Ethers.
- 2 Marks and 3 Marks Questions were asked from Solutions, Electrochemistry, The *p*-Block Elements, Aldehydes, Ketones and Carboxylic acids.

Thus, high weightage carrying chapters are :

- **Physical Chemistry**
 - Solutions
 - Electrochemistry
 - Chemical Kinetics
- **Inorganic Chemistry**
 - The *p*-Block Elements
 - The *d*- and *f*-Block Elements
- **Organic Chemistry**
 - Haloalkanes and Haloarenes
 - Alcohols, Phenols and Ethers
 - Aldehydes, Ketones and Carboxylic Acids
 - Amines

Also prepare other chapters like Surface Chemistry, Coordination Compounds, Biomolecules, Polymers and Chemistry in everyday life as from these chapters 2 or 3 marks questions are being asked for sure.

Refer to MTG CBSE Champion for Chemistry which will help you to know the weightage of topics of a particular chapter and to look into the pattern of questions asked in last 10 years.

V After class-12 I tried to crack medical entrance exams like NEET/AIIMS but I did not succeed. Now I want to target these Exams once again. Please suggest me books that will really help me to achieve my goals.

(Ishita Das, West Bengal)

Don't get disheartened! To crack any exam study smartly with your full potential. Follow a planned strategy, firstly it is necessary to know the types or the pattern of the questions that are asked in the exam. For this MTG previous years' question bank of NEET/AIPMT (32 years) & AIIMS (26 years) will help you in which completely solved chapterwise questions are given.

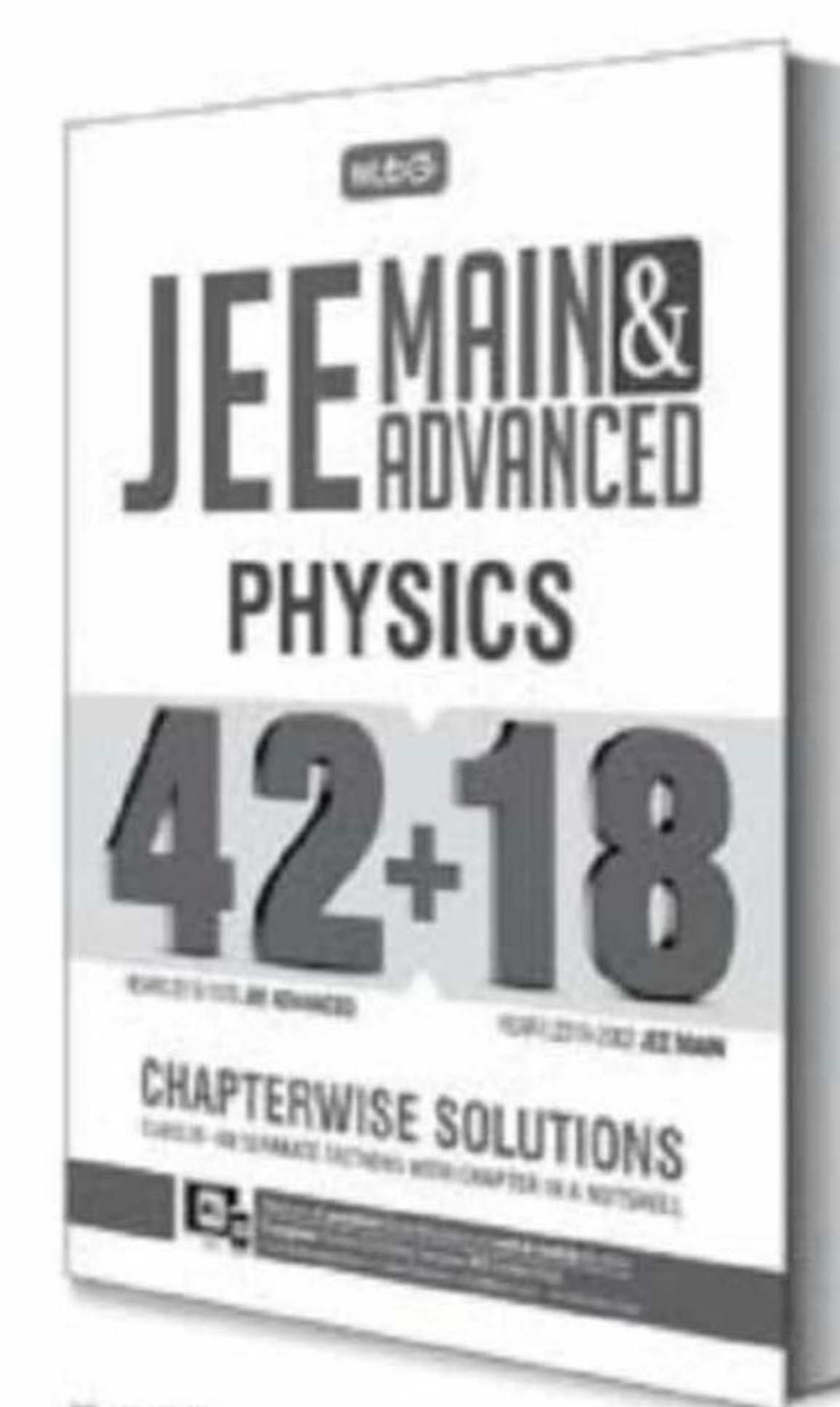
Other reference books like MTG NCERT at your Fingertips & NEET Guide Series will give you the strong base for the preparation. As in NEET exam, Biology is the highest weightage carrying subject so for the conceptual clarity you can refer to MTG Count on Me Biology for Class 11 & 12 also.

All the Best 🍀

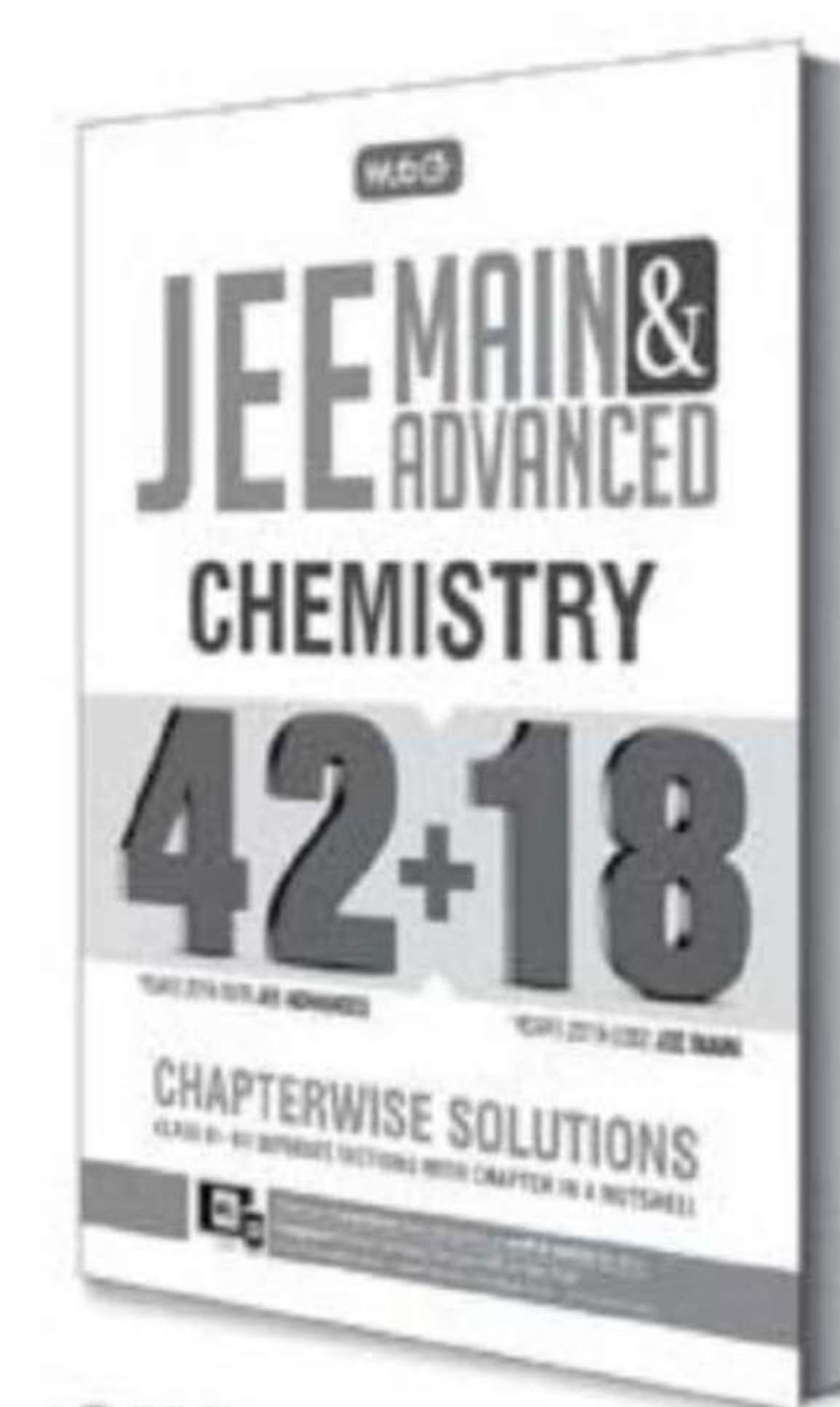
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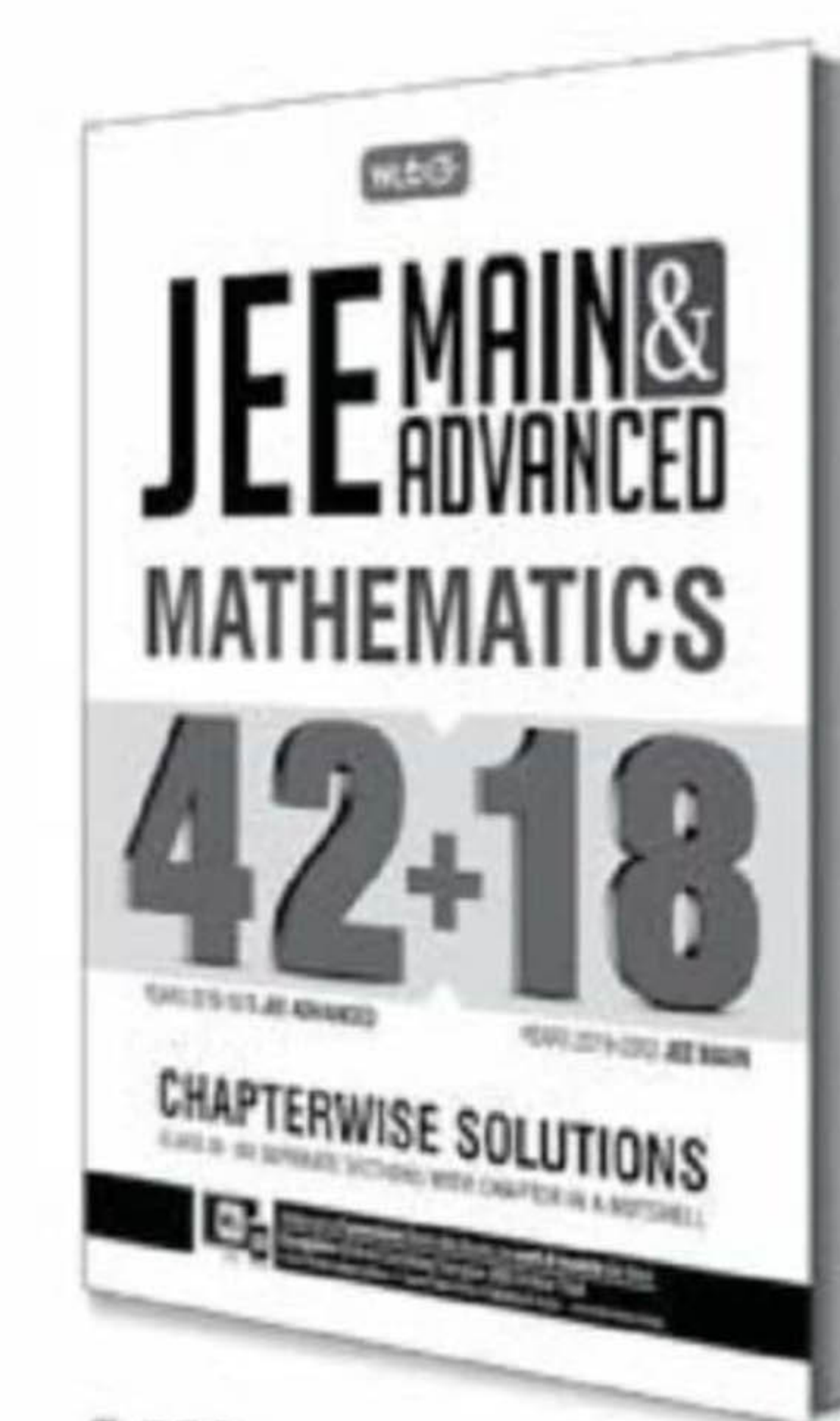
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Rank Enhancer

HYBRIDISATION

Process of intermixing of atomic orbitals of same energy or nearly same energy to give same number of new orbitals having same shape, energy and size is called Hybridisation and such orbitals formed are called as "Hybrid orbitals".

Requirement :

- To form all bonds of same length and energy.
- It decides geometry with minimum repulsion and maximum stability.

Some important basic facts of Hybridisation

- No. of hybrid orbitals formed = No. of atomic orbitals mixed
- Half-filled, fully-filled and empty orbitals can hybridise. *e.g.*,
 - In CH_4 , all half-filled orbitals hybridise. In NH_3 one fully-filled and 3 half-filled orbitals hybridise.

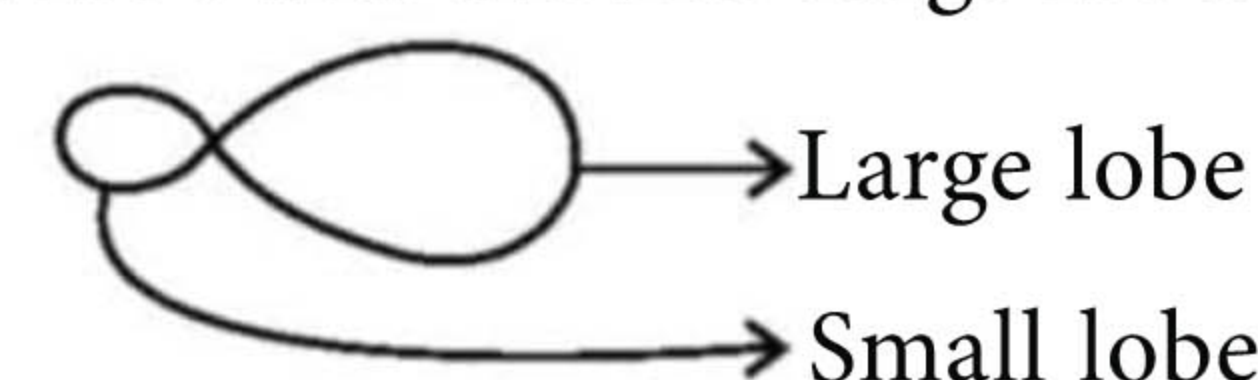
- In B_2H_6 , one empty orbital and 3 half-filled orbitals hybridise.

- Only σ and lone pairs of electrons participates in hybridisation but not π -electrons.

	σ electron	lp electron	π electron
Hybridisation	✓	✓	✗
Bond formation	✓	✗	✓

- Hybrid orbitals are named after parent orbitals. *e.g.*,
 - If one 's', three 'p' and one 'd' orbitals hybridised, then name of all five hybridised orbitals will be sp^3d .

- Shape of all hybrid orbitals will be dumbbell with one small lobe and another large lobe.



- Hybrid orbitals orient themselves in such a way that repulsive forces between them will be minimum.

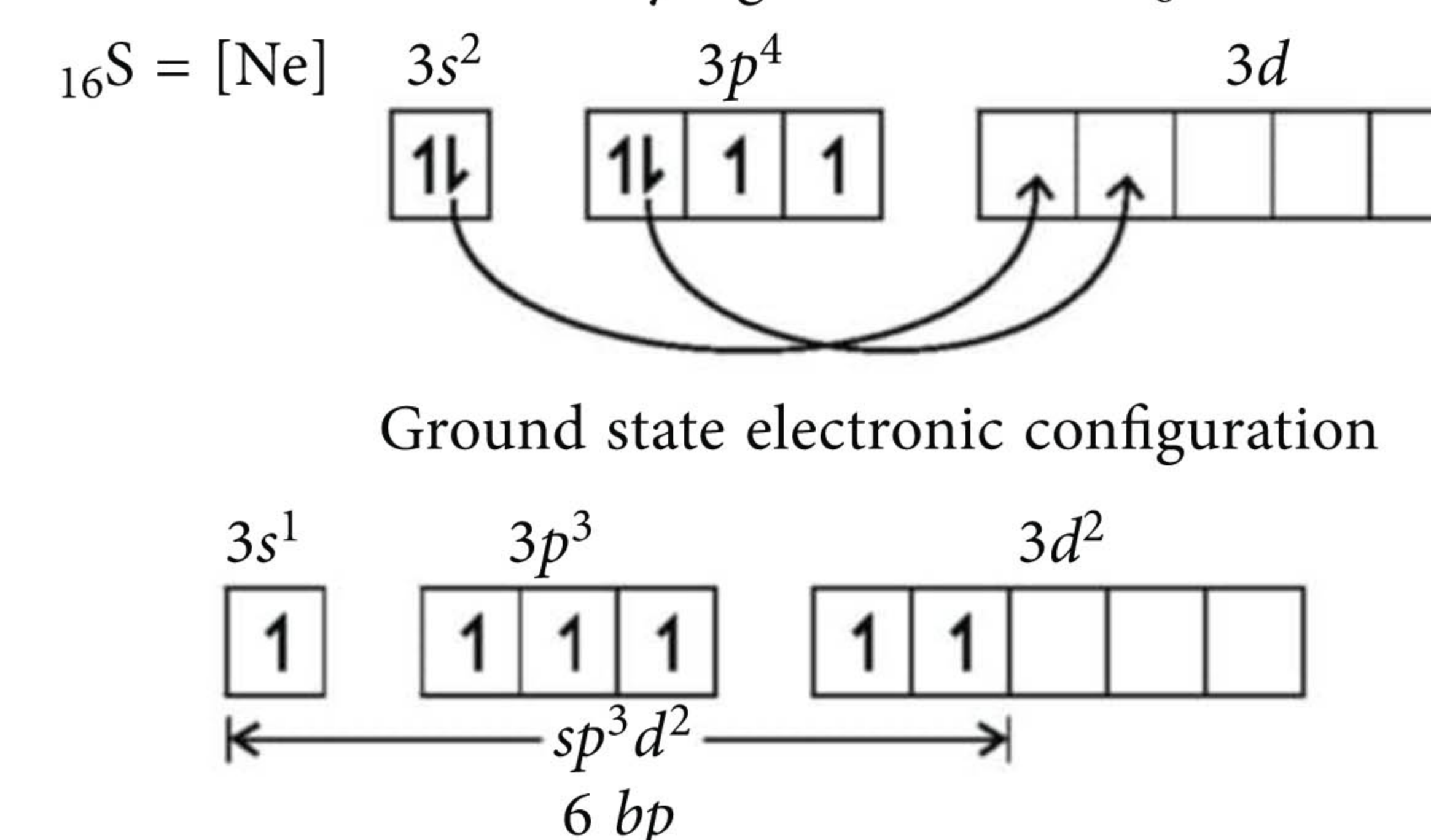
Hybridisation	Atomic orbitals	Bond pair	Lone pair	Shape	Bond angle	Example
sp	s & p	2	0	Linear	180°	HgCl_2 , BeCl_2 , C_2H_2
sp^2	s & two p	3	–	Triangular planar	120°	BCl_3 , C_2H_4 , NO_3^- , CO_3^{2-} , CH_3^+
		2	1	Bent (or) 'V' (or) Angular	–	CCl_2 (Dichloro carbene)
sp^3	s & three p (p_x , p_y & p_z)	4	–	Tetrahedral	$109^\circ 28'$	CH_4 , NH_4^+ , SnCl_4
		3	1	Pyramidal	–	NH_3 , H_3O^+ , CH_3^-
		2	2	Bent (or) 'V' (or) Angular	–	H_2S , SCl_2 , SO_2 , I_3^+

By K. Vijay Bhasker, Senior faculty at Sri Chaitanya Educational Institution, Visakhapatnam

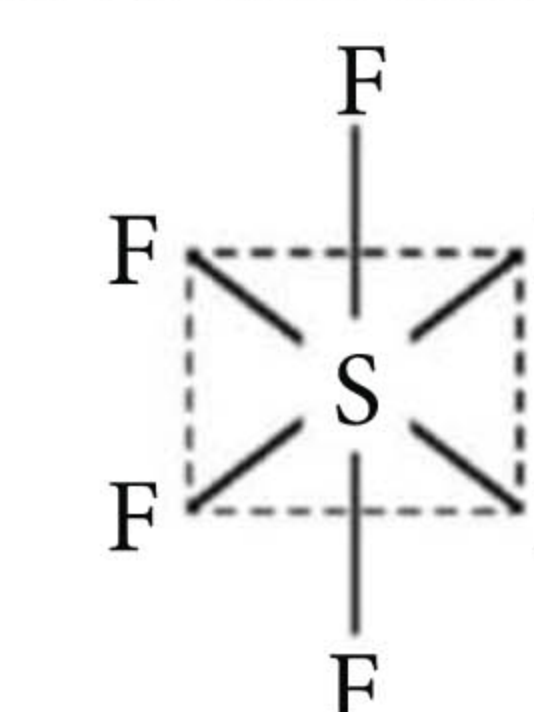
sp^3d	$s, p_x, p_y \text{ \& } p_z, d_{z^2}$	5	–	Triangular bipyramidal	$120^\circ \text{ \& } 90^\circ$	PCl_5
		4	1	See-saw	–	SF_4
		3	2	T-shaped	–	ClF_3
		2	3	Linear	180°	I_3^-
sp^3d^2	$s, p_x, p_y, p_z, d_{x^2-y^2}, d_{z^2}$	6	–	Octahedral	90°	SF_6 , $[\text{CrF}_6]^{3-}$
		5	1	Square pyramidal	–	BrF_5
		4	2	Square planar	90°	XeF_4
sp^3d^3	$s, p_x, p_y, p_z, d_{xy}, d_{yz} \text{ \& } d_{zx}$	7	–	Pentagonal bipyramidal	$72^\circ \text{ \& } 90^\circ$	IF_7
dsp^2	$d_{x^2-y^2}, s, p_x, p_y$	4	0	Square planar	90°	$[\text{Ni}(\text{CN})_4]^{2-}$

Examples :

- Molecule with only sigma-bonds : SF_6

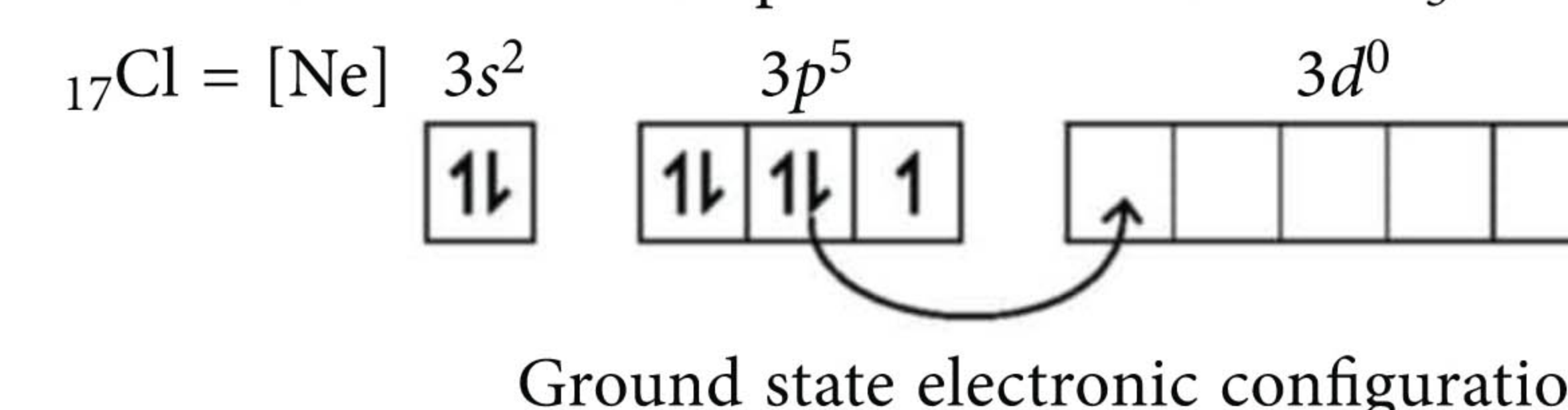


- 2nd Excited state electronic configuration [Excited state decided by number of unpaired electrons required]



Octahedral

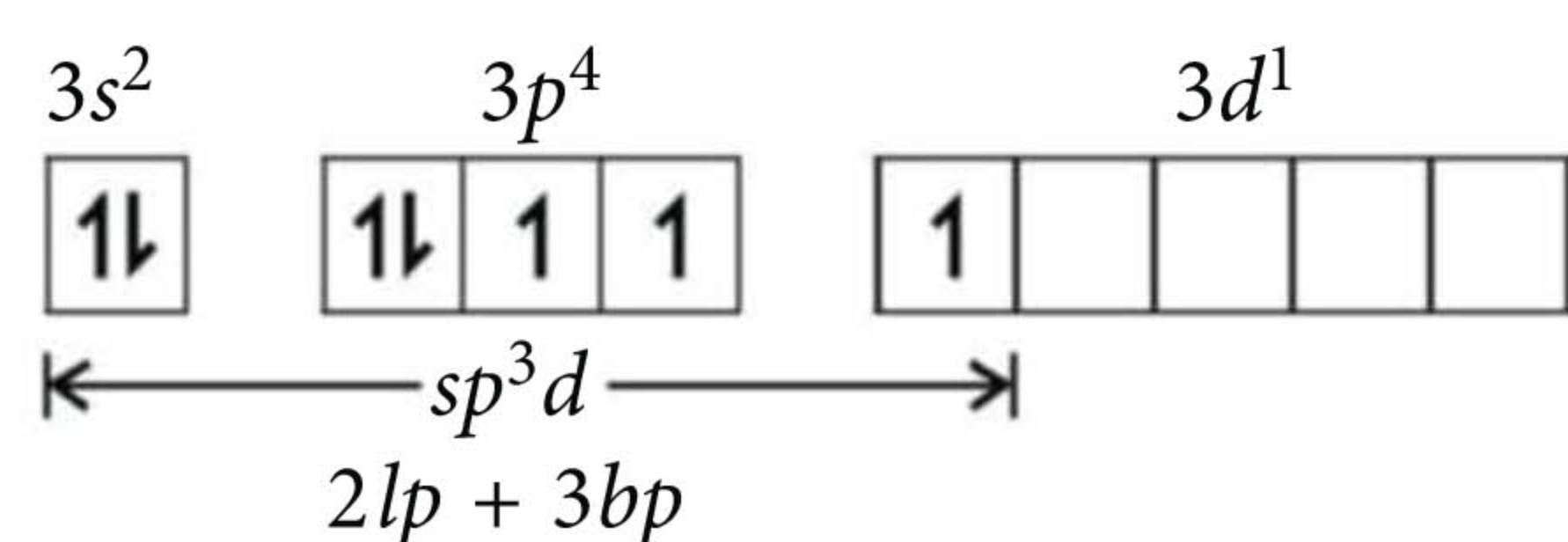
- Molecule with lone pair and σ -bonds : ClF_3



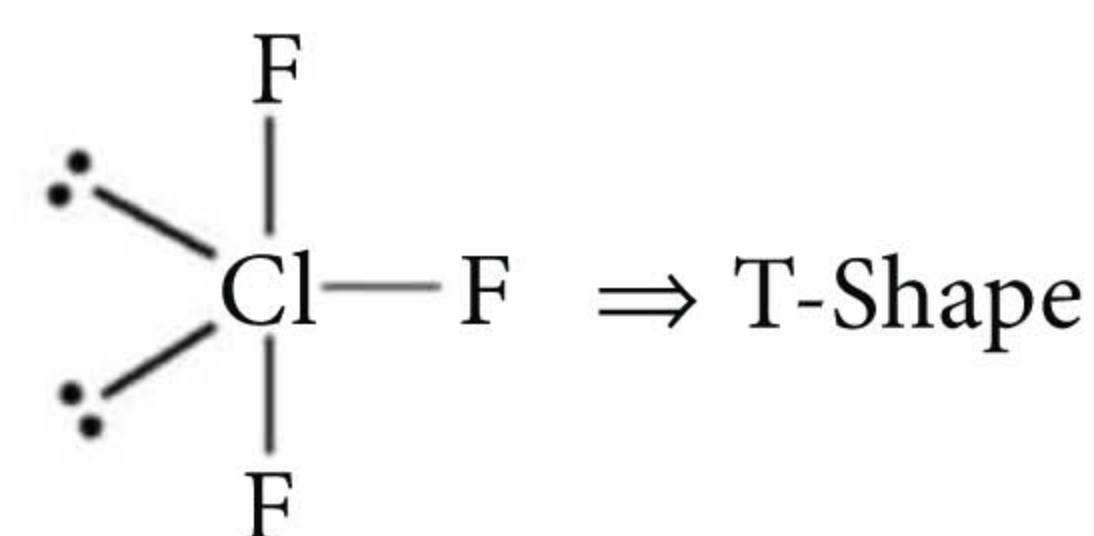
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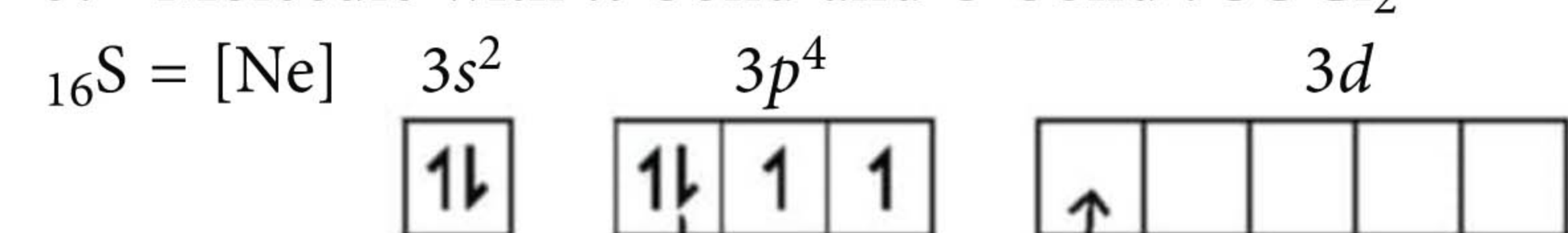


1st excited state electronic configuration

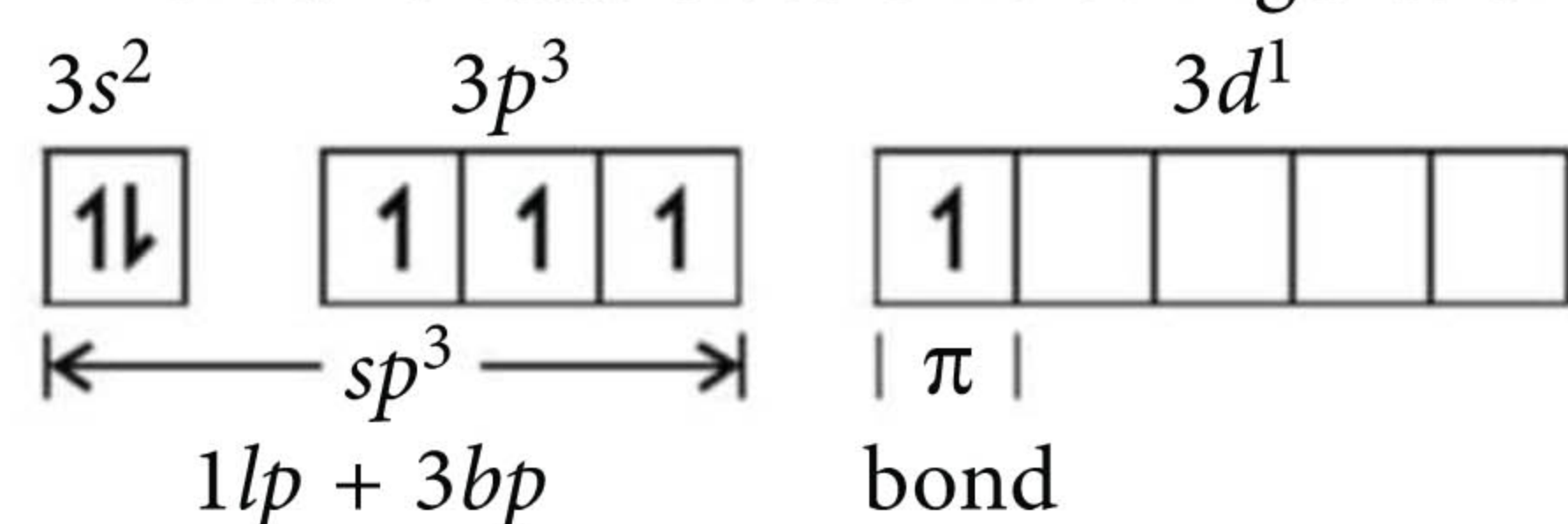


Note : Lone pairs to be kept at a place with maximum possible bond angle and minimum repulsion.

3. Molecule with π -bond and σ -bond : SOCl₂

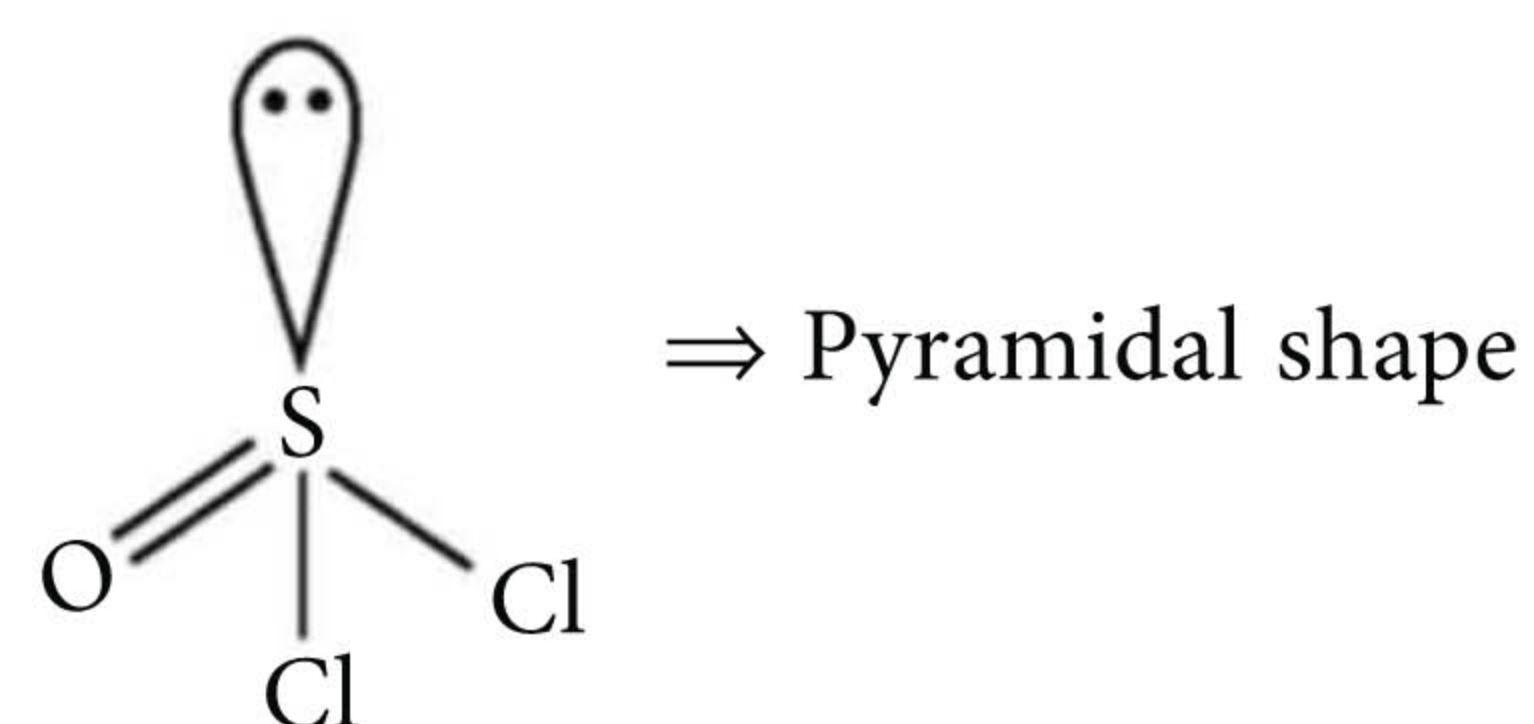


Ground state electronic configuration

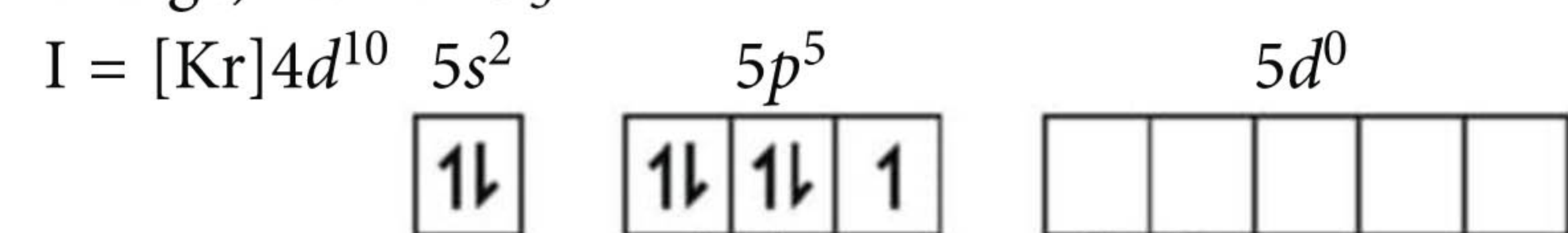


π-bond type = pπ - dπ

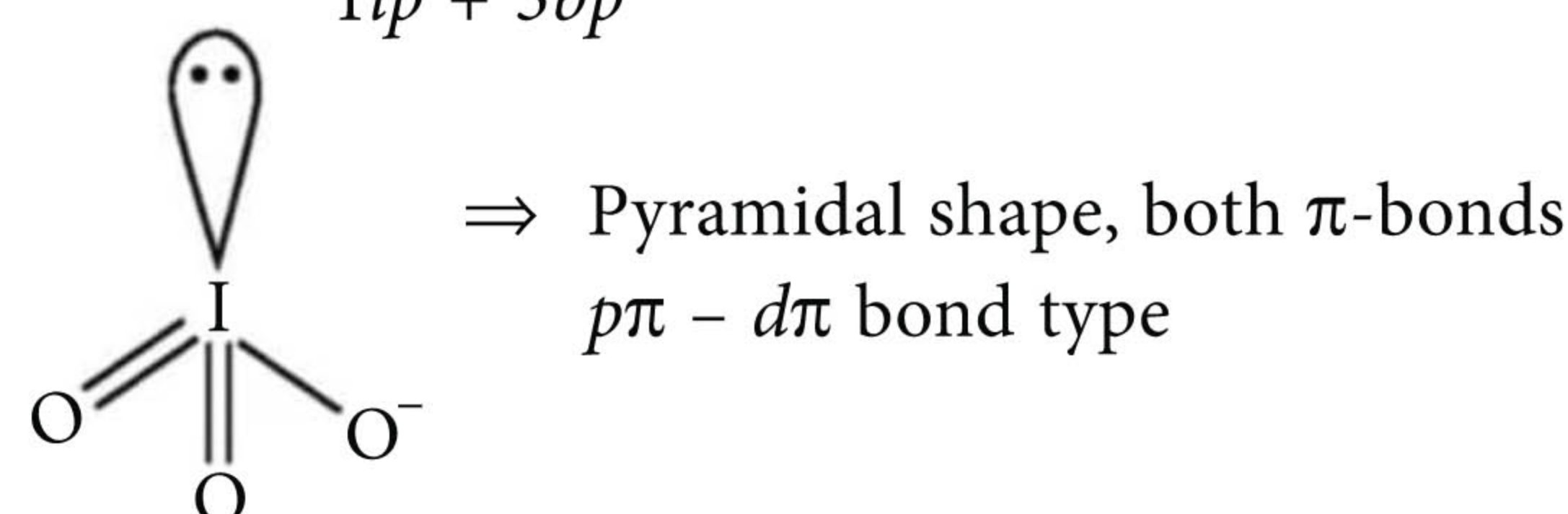
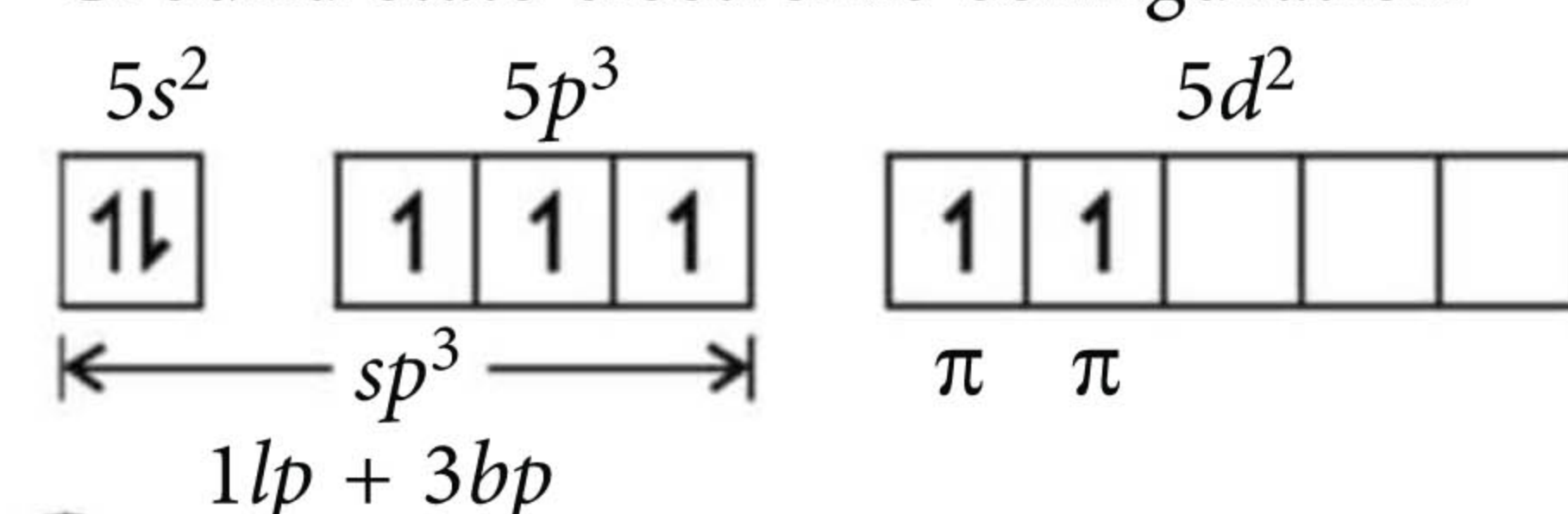
1st excited state configuration



4. In complex ions (π -Bond, lone pair, σ -Bond and charge) 4d¹⁰ : IO₃⁻



Ground state electronic configuration



Shortcut : Hybridisation = No. of σ -bonds + No. of lp

Example :

1. XeF₂ → 8e⁻ of Xe in valence shell ⇒ 2 σ -bonds and remaining 6e⁻ make 3 lp

∴ 2 + 3 = 5 = one s + three p + one d = sp³d

2. SO₂ → 6e⁻ in valence shell ⇒ 2 σ -bond + 2π-bonds remaining 2e⁻ make 1 lp

∴ 2σ + 1 lp = 3 ⇒ one s + two p = sp²

3. ClO₂ → 7e⁻ in valence shell ⇒ 2 σ -bond + 1 π-bond remaining 4e⁻ make 2 lp

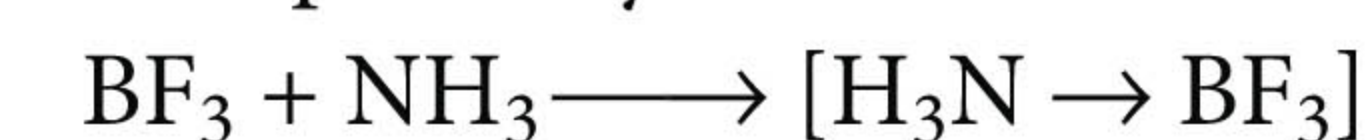
⇒ 2σ + 2 lp = 4 = one s + three p = sp³

QUESTIONS FOR PRACTICE

Single Option Correct Type

- Geometry of [BeF₄]²⁻ is
(a) square planar (b) see-saw
(c) tetrahedral (d) trigonal pyramidal.
- Shape and number of lp in HCP molecule are
(a) bent and 1 (b) linear and 3
(c) linear and 1 (d) bent and 3
- Sequence of hybridisation of 'C' atoms in allene is
(a) sp³, sp², sp³ (b) sp², sp, sp²
(c) sp, sp², sp (d) sp², sp², sp²
- Size of hybrid orbitals decreases in the order of
(a) sp > sp² > sp³ (b) sp³ > sp > sp²
(c) sp² > sp > sp³ (d) sp³ > sp² > sp
- In which of the following pairs, central atoms have same hybridisation?
(a) CO₂ and SO₂ (b) PCl₃ and ICl₃
(c) H₂O and SCl₂ (d) SO₃ and SO₃²⁻
- Type(s) of hybridisation of 'C' in C₂(CN)₄ is/are
(a) sp only (b) sp² only
(c) sp and sp² (d) sp, sp² and sp³
- In which of the following all bond lengths are not equal?
(a) SiF₄ (b) SCl₄
(c) BF₄⁻ (d) XeF₄
- Which of the following pairs of molecules/ions are isostructural having different hybridisation?
(a) SO₄²⁻, SO₃²⁻ (b) BeCl₂, BCl₃
(c) BeCl₂, I₃⁻ (d) SO₂, CO₂
- Number of hybrid orbitals in 'N' of ammonium ion, amide ion and ammonia are respectively
(a) 4, 2, 3 (b) 4, 2, 2
(c) 2, 4, 4 (d) 4, 4, 4

10. State of hybridisation of 'B' in reactant and product is respectively

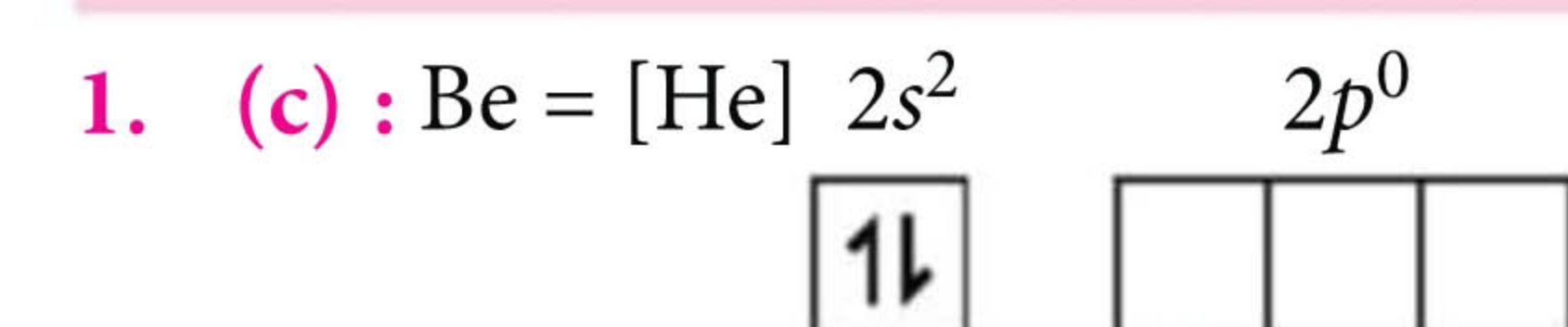


- (a) sp² and sp² (b) sp³ and sp³
(c) sp² and sp³ (d) sp³ and sp²

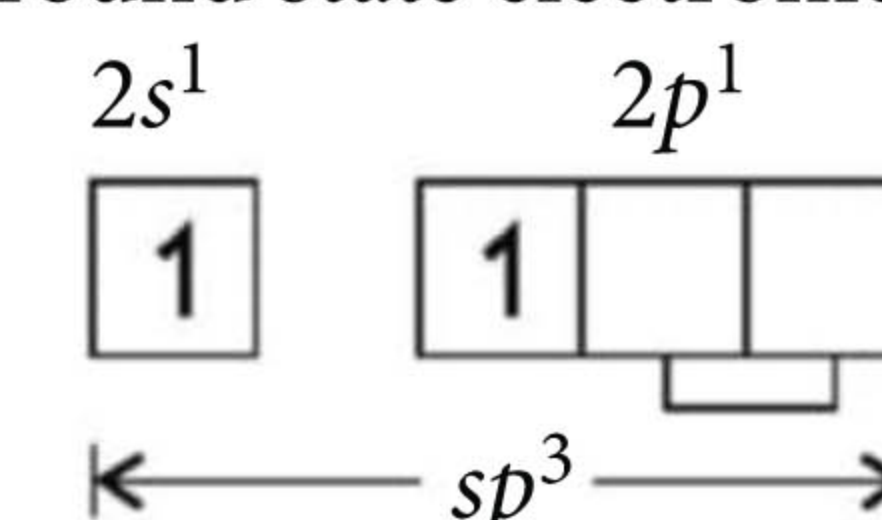
Integer Type

- Number of tetrahedral angles in CCl₄ is
- Number of right angles in BrF₅ is
- If number of lone pairs in IF₄⁻ is 2n, then n is
- Number of dπ-pπ bonds in SO₂ is
- Number of tetrahedral angles in CCl₂F₂ is

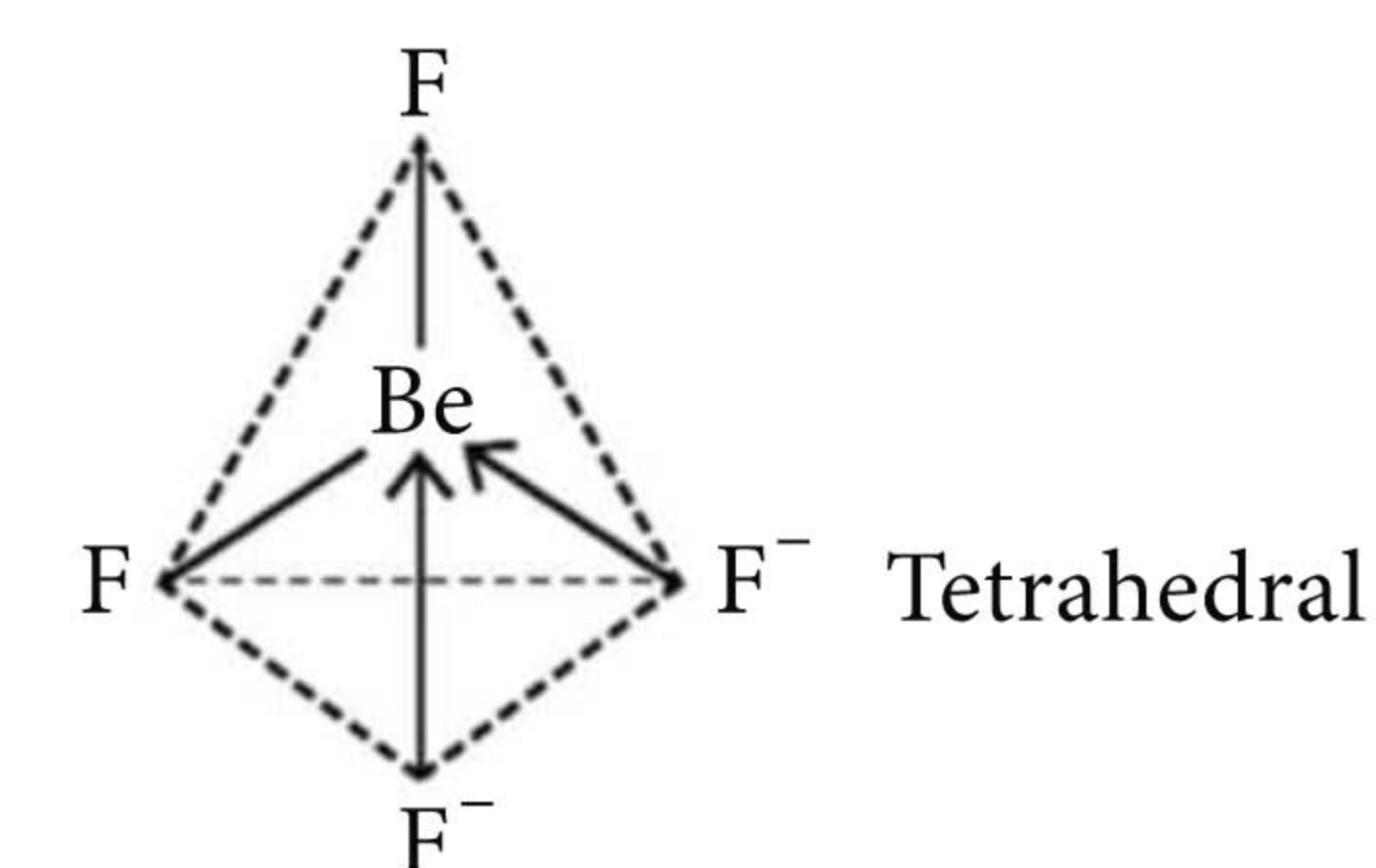
Hints & Solutions



Ground state electronic configuration



For coordinate covalent bond empty orbitals hybridises

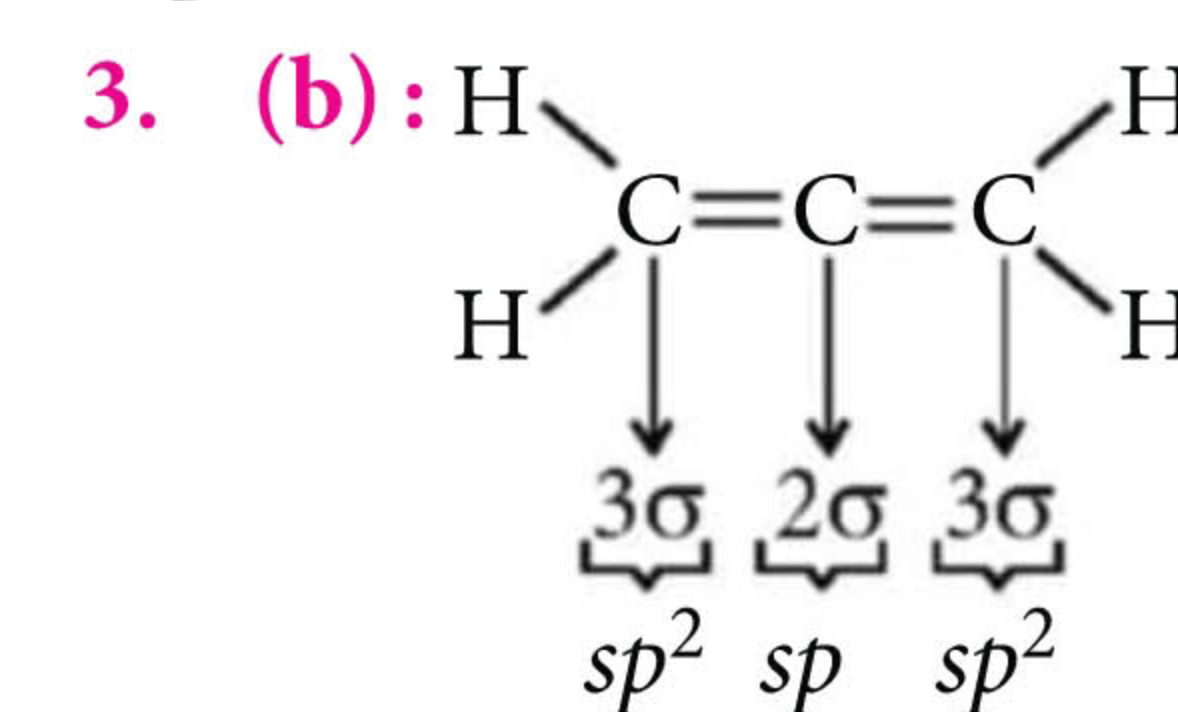


2. (c) : H—C≡P:

2 σ -Bond and no lp on central carbon atom

∴ sp hybridisation linear shape

1 lp on P is available.



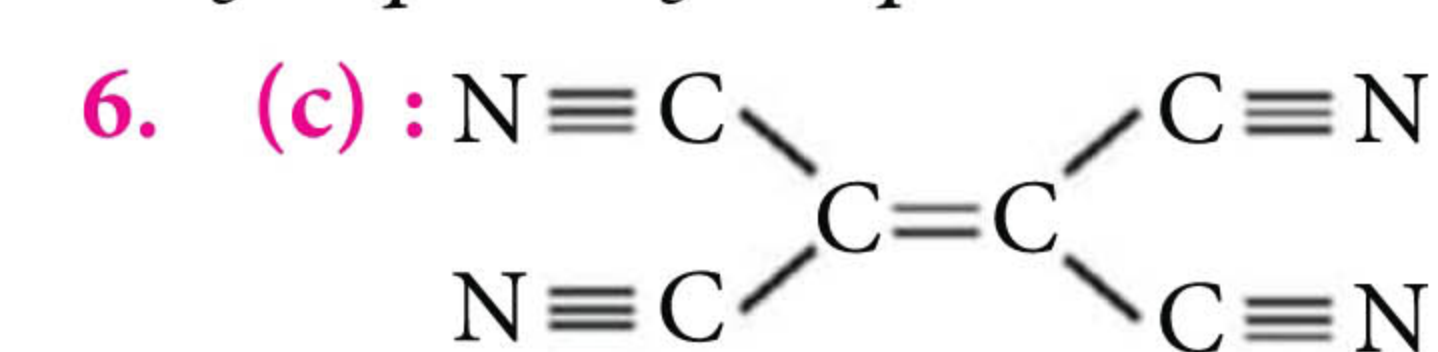
4. (d) : Size of hybrid orbital ∝ No. of orbitals hybridise

5. (c) : CO₂ = sp, SO₂ = sp²

PCl₃ = sp³, ICl₃ = sp³d

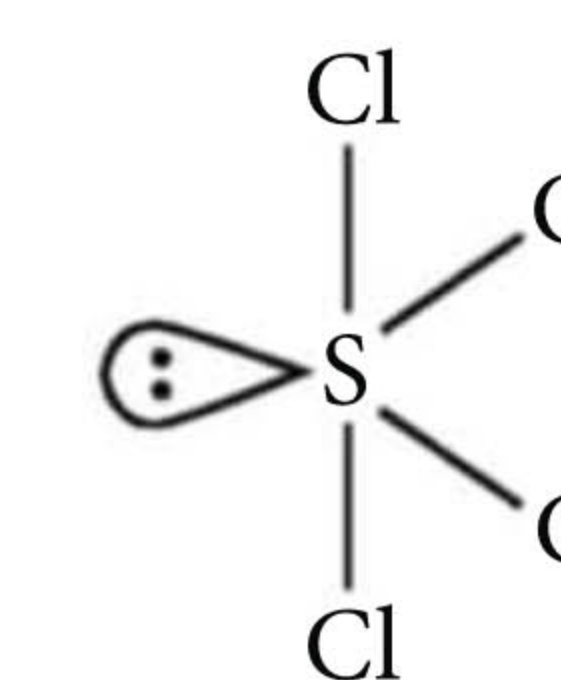
H₂O and SCl₂ = sp³

SO₃ = sp², SO₃²⁻ = sp³

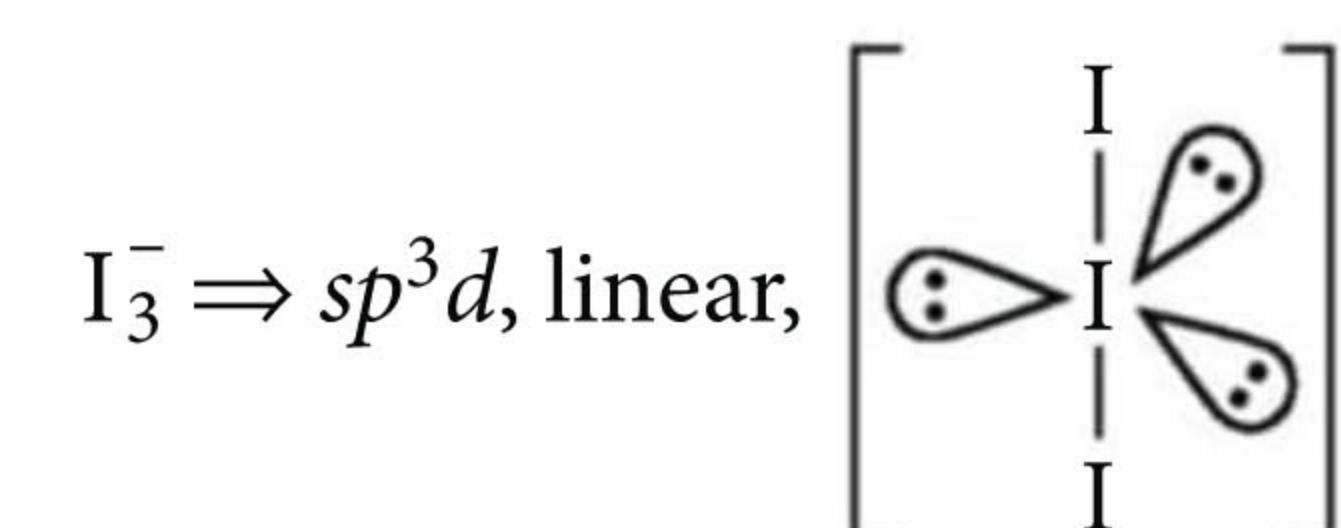


7. (b) : In SCl₄ (see-saw structure)

axial bond length > equatorial bond length.



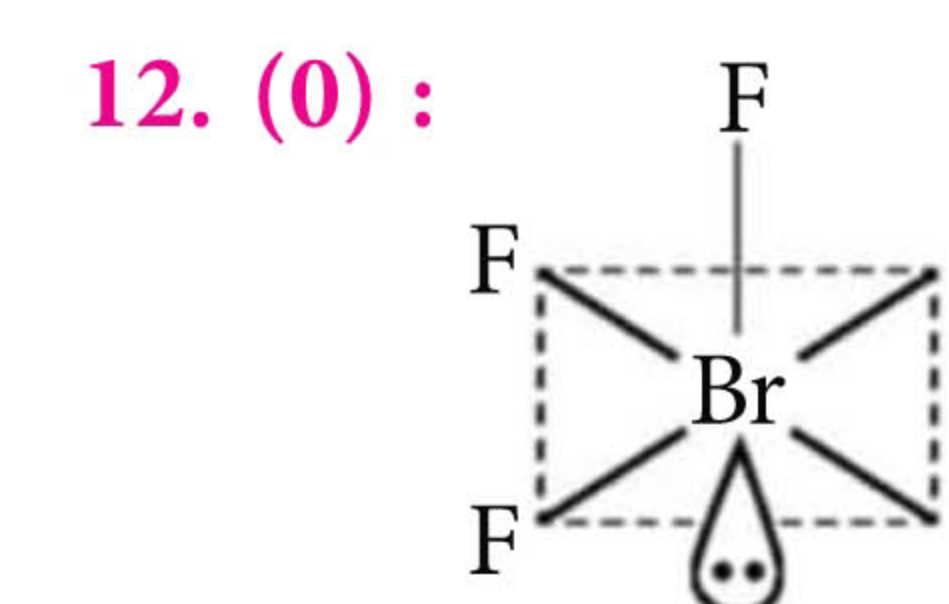
8. (c) : BeCl₂ ⇒ sp², linear, Cl—Be—Cl



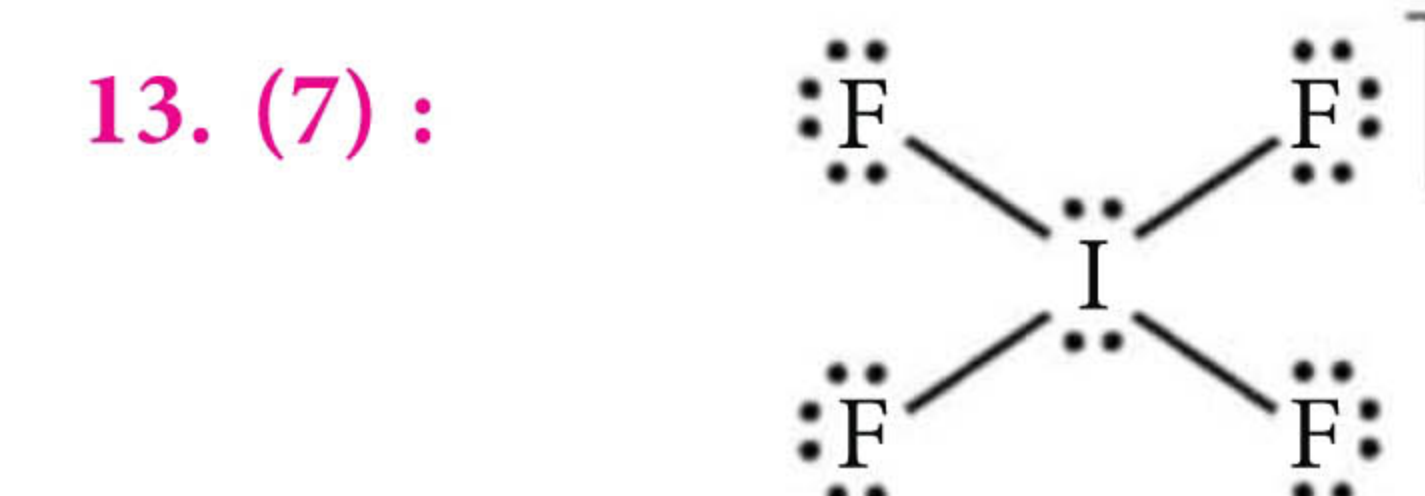
9. (d) : Lone pairs also participate in hybridisation.



11. (6) : 6 tetrahedral angles are formed.

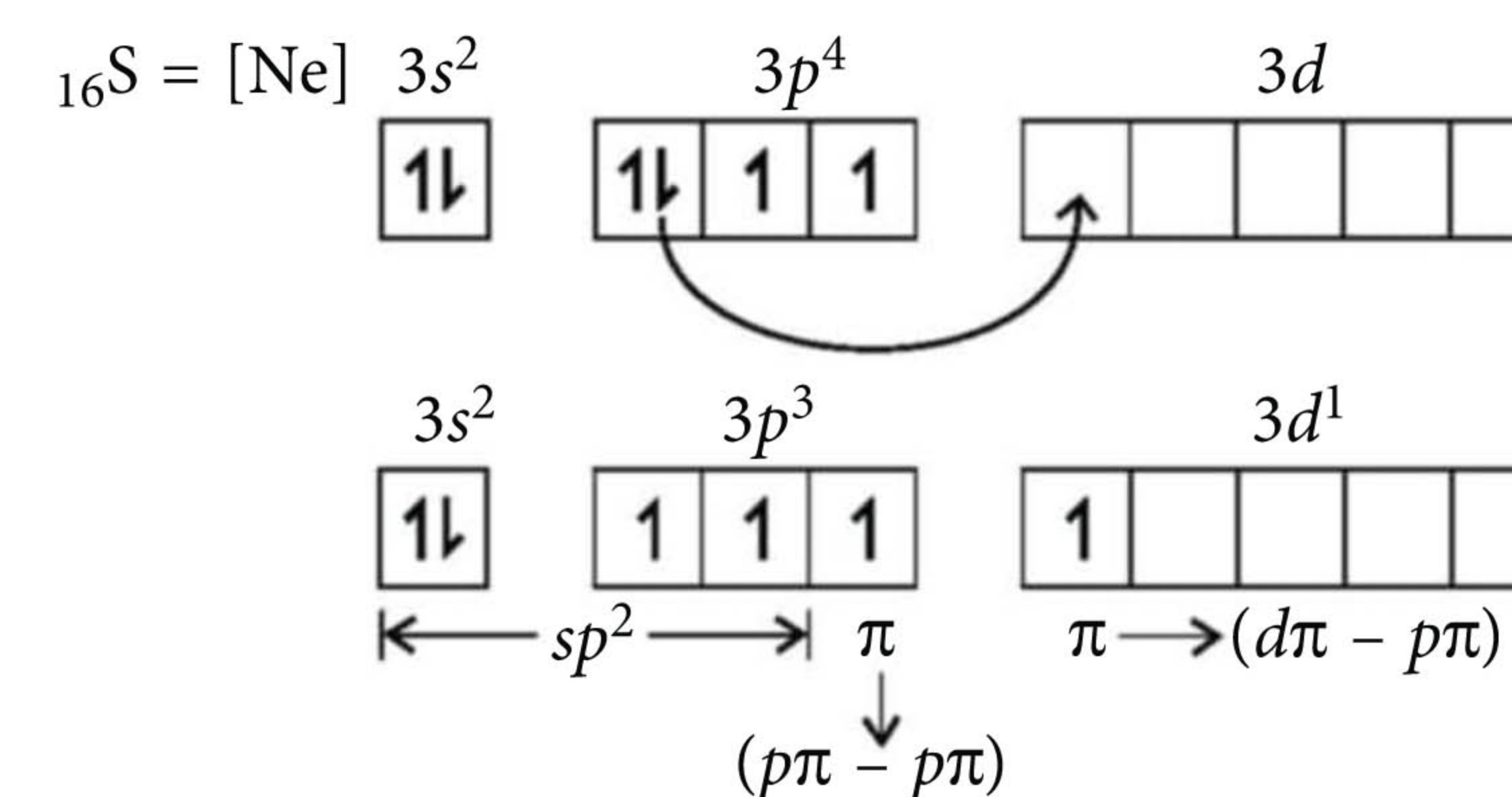


Due to more repulsion from bottom, 90° angles not maintained.



3lp on 4 F + 2 lp on I = 14 = 2 × 7

14. (1) :

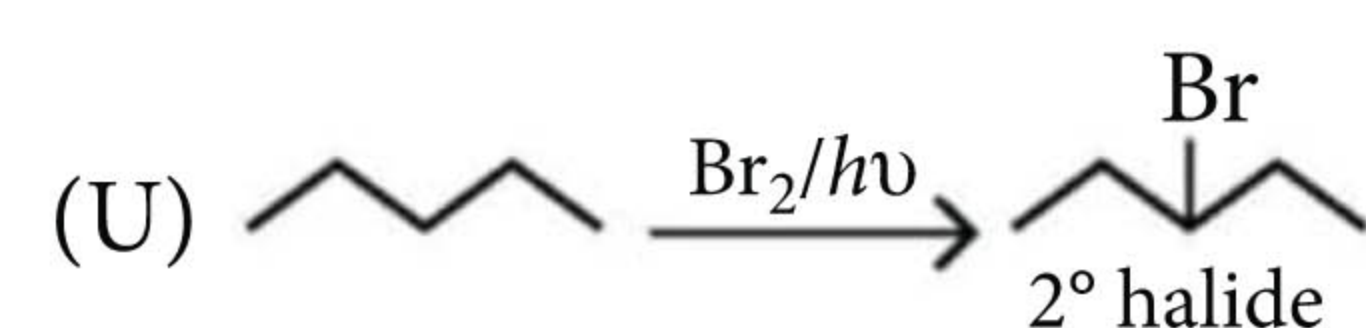
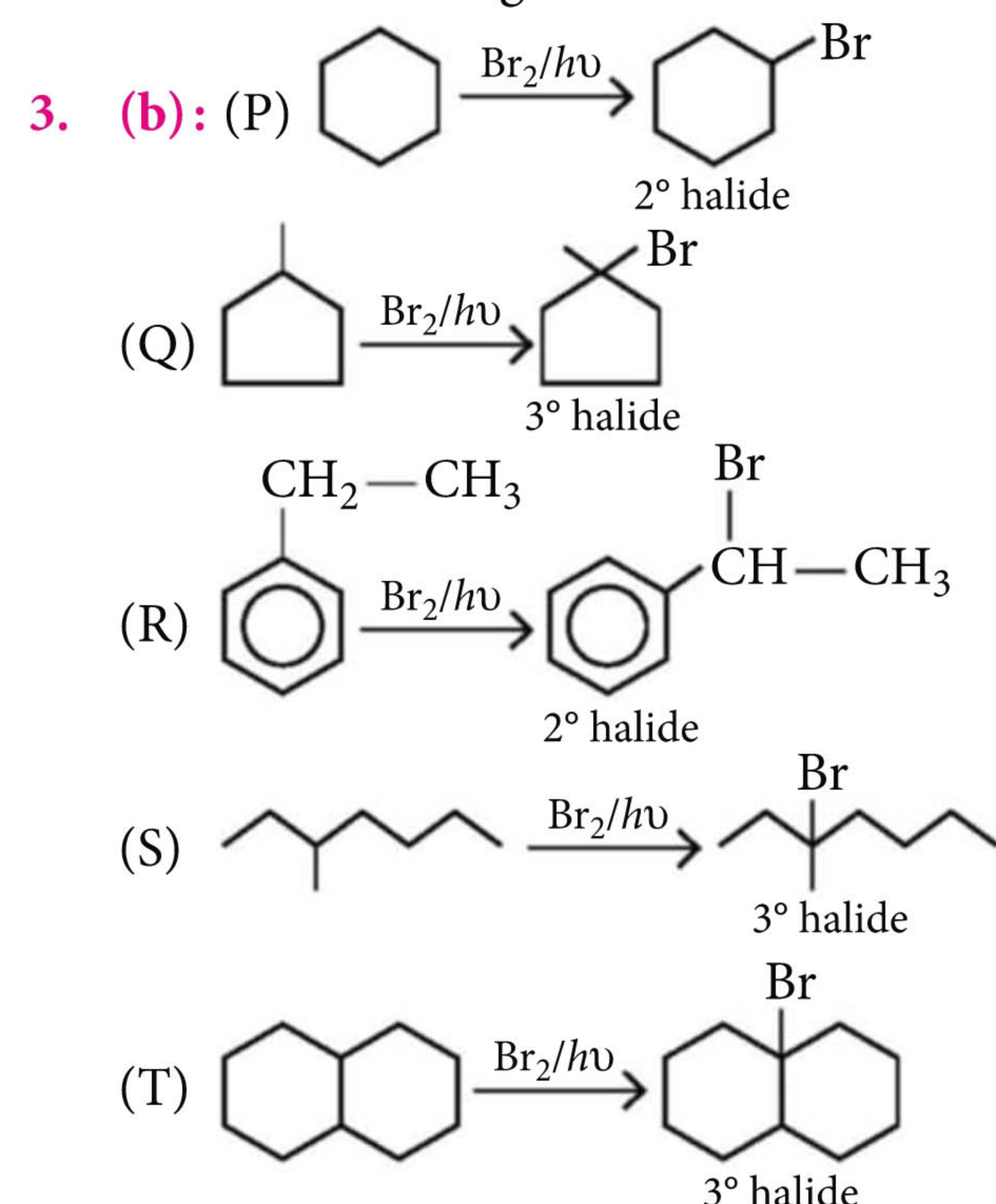


15. (0) : Due to difference in size of Cl and F, same bond angle cannot be maintained.

CHEMISTRY MUSING

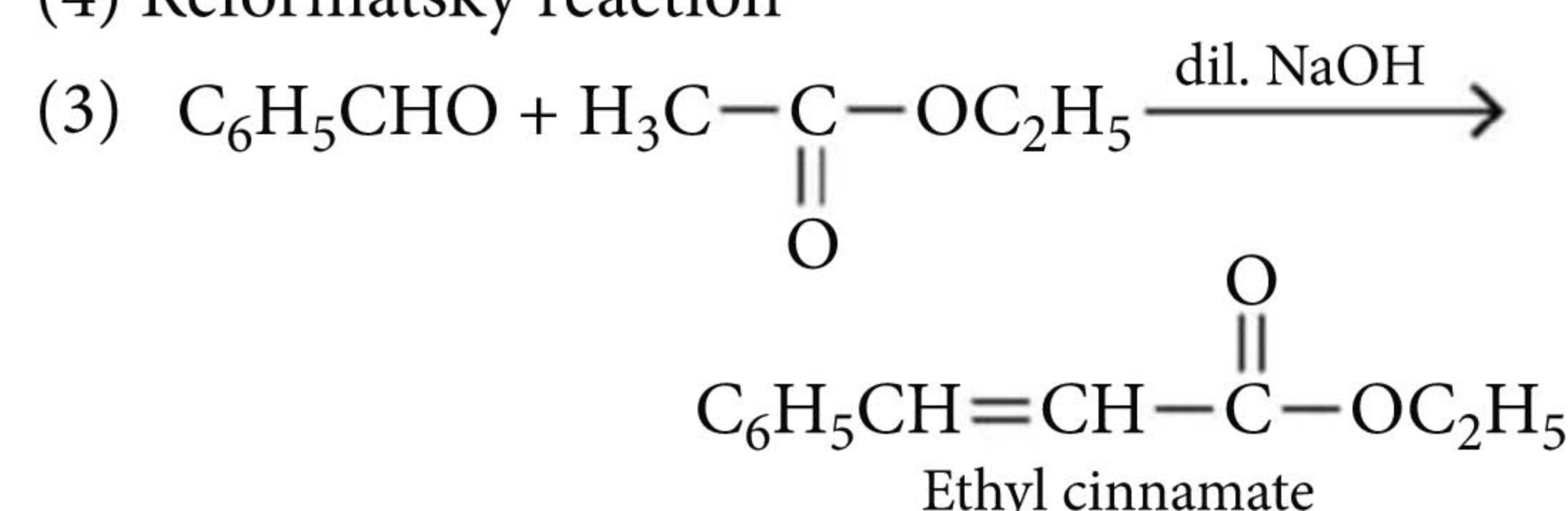
SOLUTION SET 73

1. (c): $5\text{I}^- + \text{IO}_3^- + 6\text{H}^+ \longrightarrow 3\text{I}_2 + 3\text{H}_2\text{O}$
 $\frac{\text{Moles of KI used}}{\text{Moles of KIO}_3 \text{ used}} = 5$
 (a) For 0.004 mole of KIO_3 , moles of KI required
 $= 0.004 \times 5 = 0.02 = 0.1 \times V_L$
 $\therefore V_L = 0.2 \text{ L} = 200 \text{ mL}$
 (b) For 0.006 mole of H_2SO_4 (0.012 mole of H^+),
 moles of KI required $= \frac{0.012 \times 5}{6} = 0.01 = 0.1 \times V_L$
 $\therefore V_L = 0.1 \text{ L} = 100 \text{ mL}$
 (c) From 0.5 L of KI solution ($n_{\text{KI}} = 0.05$), moles of
 I_2 produced $= \frac{0.05 \times 3}{5} = 0.03$
 (d) Valency factor of $\text{KIO}_3 = 5(\text{IO}_3^- \rightarrow \text{I}_2)$
 $\therefore E_{\text{KIO}_3} = \frac{\text{Mol. wt.}}{5}$
2. (b): (1) The total conc. of species in MgCl_2 solution will be 0.3 M and in NaCl solution it will be 0.2 M. Glucose is a non-electrolyte, hence concentration of glucose solution will be 0.1 M.
 (2) Density is defined as mass per unit volume and volume of the solution varies with temperature.
 (4) In solution, $\text{K}_4\text{Fe}(\text{CN})_6$ ionizes as
 $\text{K}_4\text{Fe}(\text{CN})_6 \rightarrow 4\text{K}^+ + \text{Fe}(\text{CN})_6^{4-}$
 Hence, the limiting value of van't Hoff factor will be 5.



4. (b): Reactions 1, 2 and 4 give cinnamic acid as these are:

- (1) Perkin reaction
 (2) Knoevenagel reaction
 (4) Reformatsky reaction



5. (a): Since $[\text{Ag}(\text{NH}_3)_2]^+$ is giving AgI ppt. with KI , it is less stable than AgI . But $[\text{Ag}(\text{CN})_2]^-$ is more stable. So, it will not give AgI ppt.

CHEMISTRY PUZZLE

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6. (b): (I) \rightarrow Inversion of configuration $\rightarrow \text{S}_{\text{N}}2$
 (II) \rightarrow Racemisation takes place $\rightarrow \text{S}_{\text{N}}1$
 (III) \rightarrow Retention of configuration $\rightarrow \text{S}_{\text{N}}i$
7. (c): Given reactions can be explained as
 $4\text{H}_2\text{O}_2 + \text{Ti}(\text{SO}_4)_2 \xrightarrow[\text{H}_2\text{O}]{\text{H}^+} 2\text{H}_2\text{TiO}_4 + 2\text{H}_2\text{SO}_4$ (A)
 $2\text{MnO}_4^- + 3\text{H}_2\text{O}_2 \xrightarrow[\text{(B)}]{\text{OH}^-} 2\text{MnO}_2 + 2\text{OH}^- + 3\text{O}_2 + 2\text{H}_2\text{O}$
 $\text{H}_2\text{O}_2 + 2\text{KI} + \text{H}_2\text{SO}_4 \longrightarrow \text{K}_2\text{SO}_4 + \text{I}_2 + \text{H}_2\text{O}$ (C)
 $\text{H}_2\text{O}_2 + \text{Cl}_2 \longrightarrow 2\text{HCl} + \text{O}_2$ (D) (E)
 Hence, X is H_2O_2 .
8. (b): $\text{MnO}_{2(s)} + 4\text{HCl}_{(aq)} \longrightarrow \text{Cl}_{2(g)} + \text{MnCl}_{2(aq)} + 2\text{H}_2\text{O}_{(l)}$
 (X) (D) (E)
9. (100): Let M.wt. of AO and A_2O_3 be m and n respectively.
 $\therefore m = a + 16$... (i) and $n = 2a + 48$... (ii)
 where, a is At. weight of A.
 Now suppose X and Y g of AO and A_2O_3 are present in mixture.

then $X + Y = 2.198$... (iii)
 Also Meq. of AO + Meq. of $\text{A}_2\text{O}_3 = \text{Meq. of K}_2\text{Cr}_2\text{O}_7$

$$\frac{X}{(a+16)/5} \times 1000 + \frac{Y}{(2a+48)/8} \times 1000 = 0.015 \times 6 \times 1000 \quad \dots \text{(iv)}$$

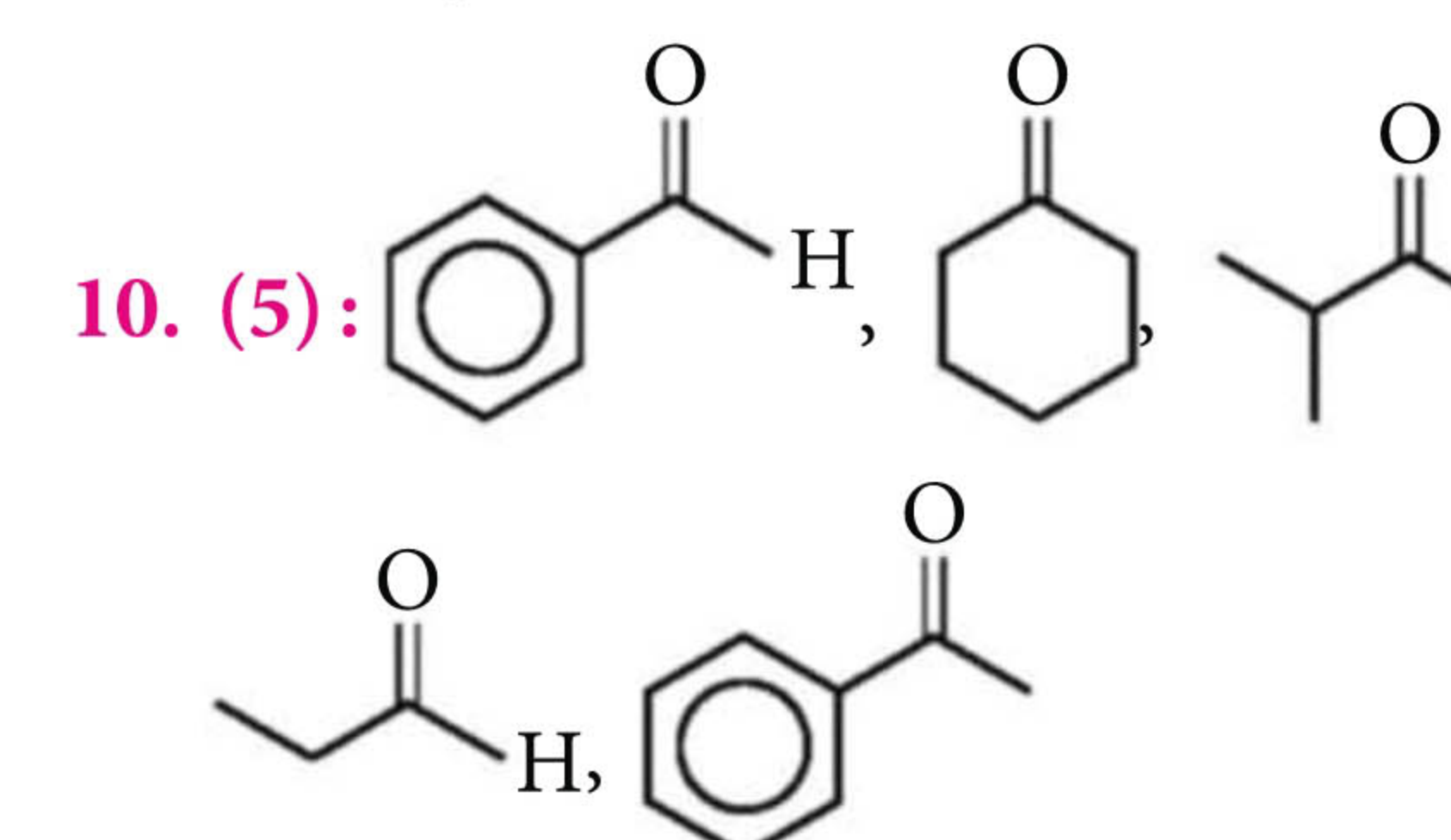
$$\therefore \begin{aligned} \text{A}^{2+} &\rightarrow \text{A}^{7+} + 5e^- \\ \text{A}_2^{3+} &\rightarrow 2\text{A}^{7+} + 8e^- \\ 6e^- + \text{Cr}_2^{6+} &\rightarrow 2\text{Cr}^{3+} \end{aligned}$$

$$\therefore \text{From Eqn. (iv), } \frac{5X}{a+16} + \frac{8Y}{2a+48} = 0.09 \quad \dots \text{(v)}$$

Also, mole of AO_4^- by AO + mole of AO_4^- by $\text{A}_2\text{O}_3 = 0.0187$

$$\frac{X}{a+16} + \frac{2Y}{2a+48} = 0.0187 \quad \dots \text{(vi)}$$

Solving eqns. (iii), (v) and (vi) $a = 100$



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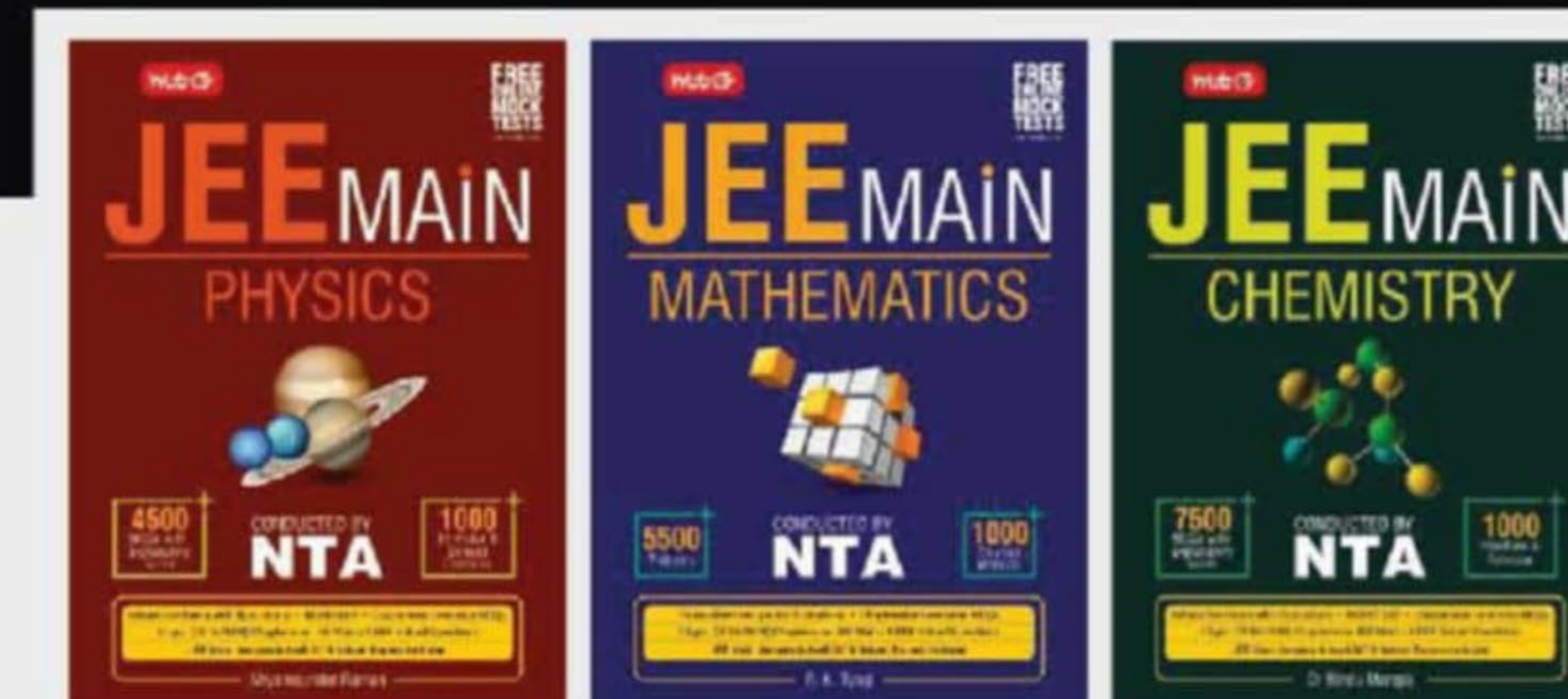
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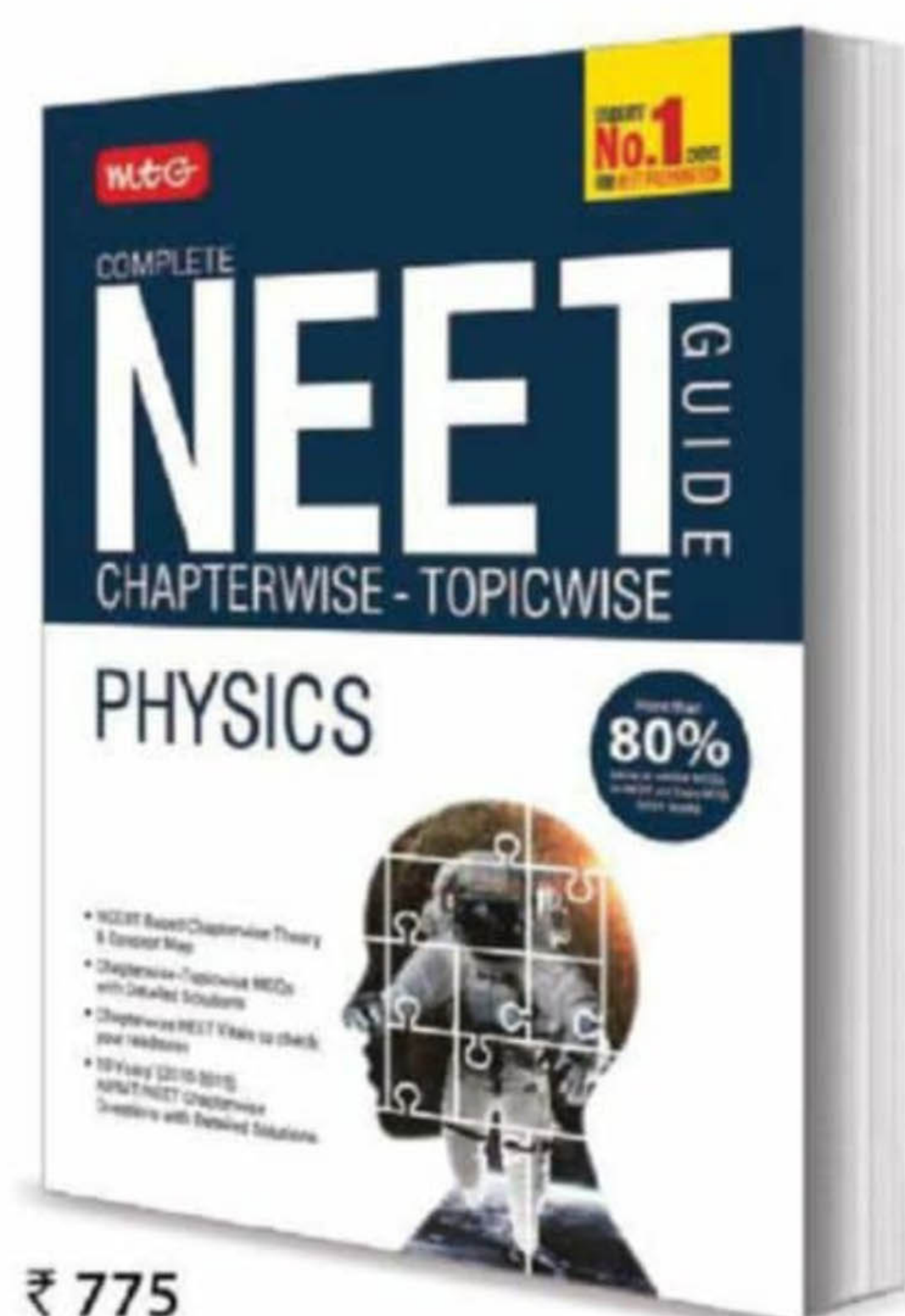
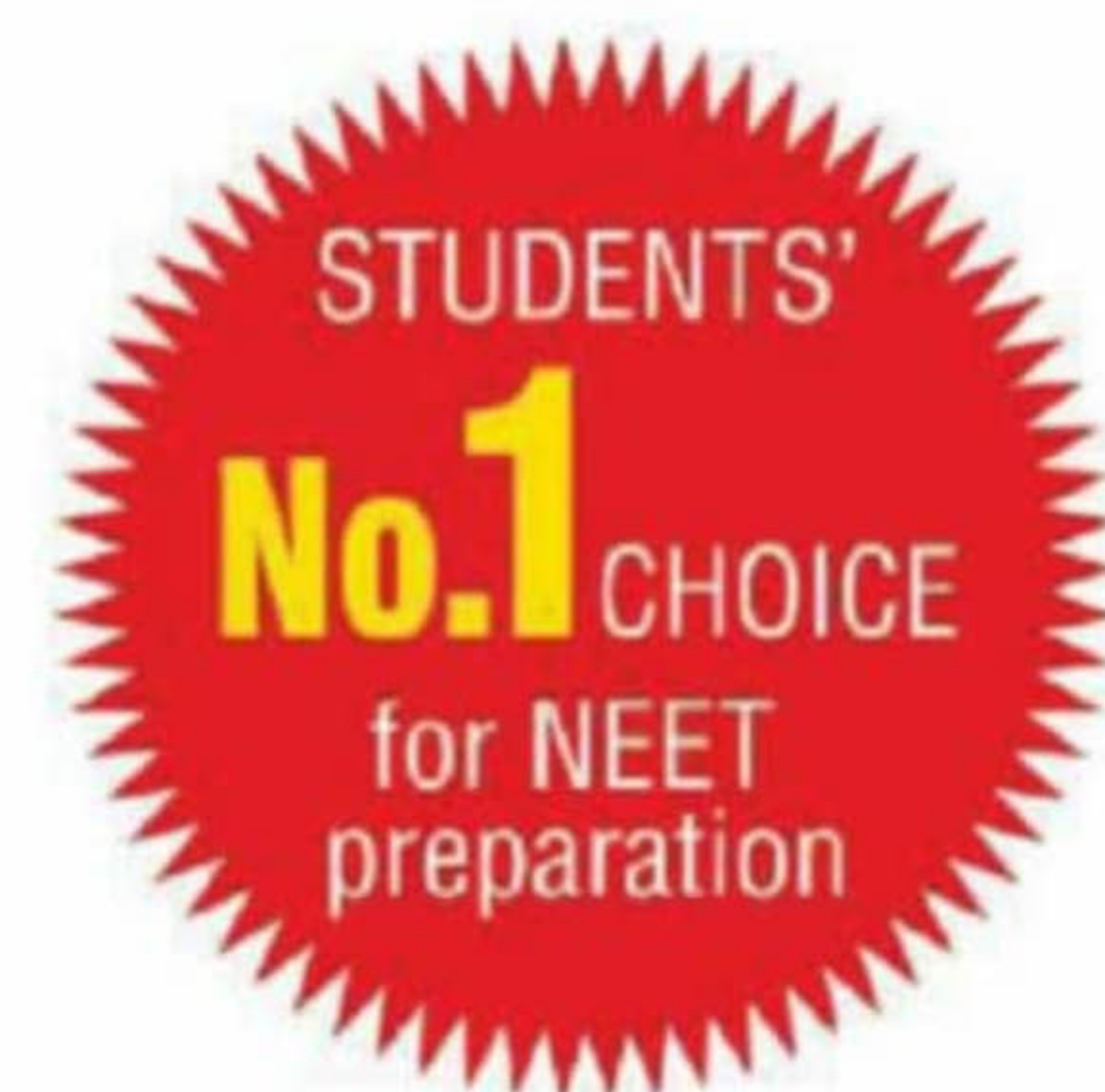
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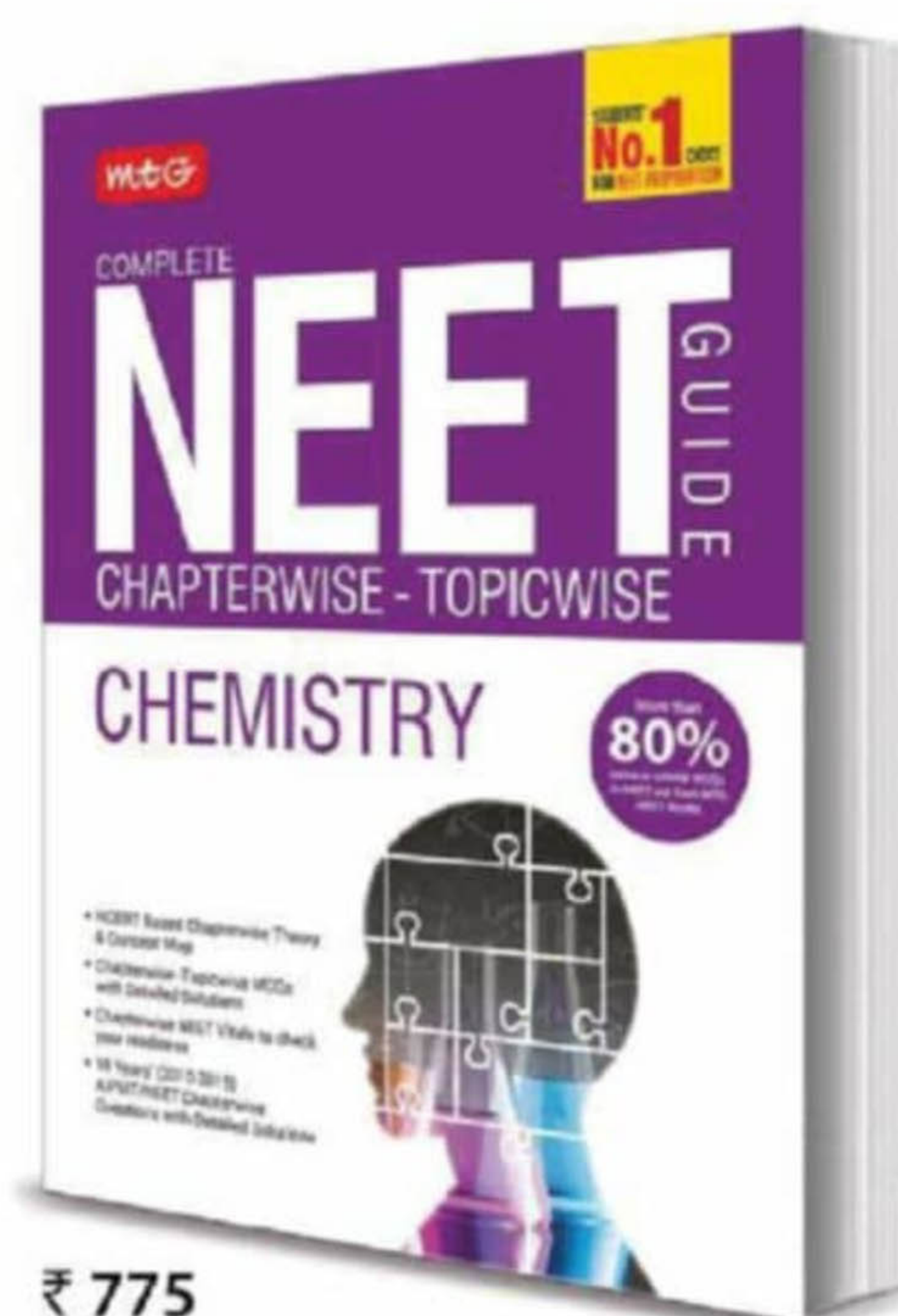
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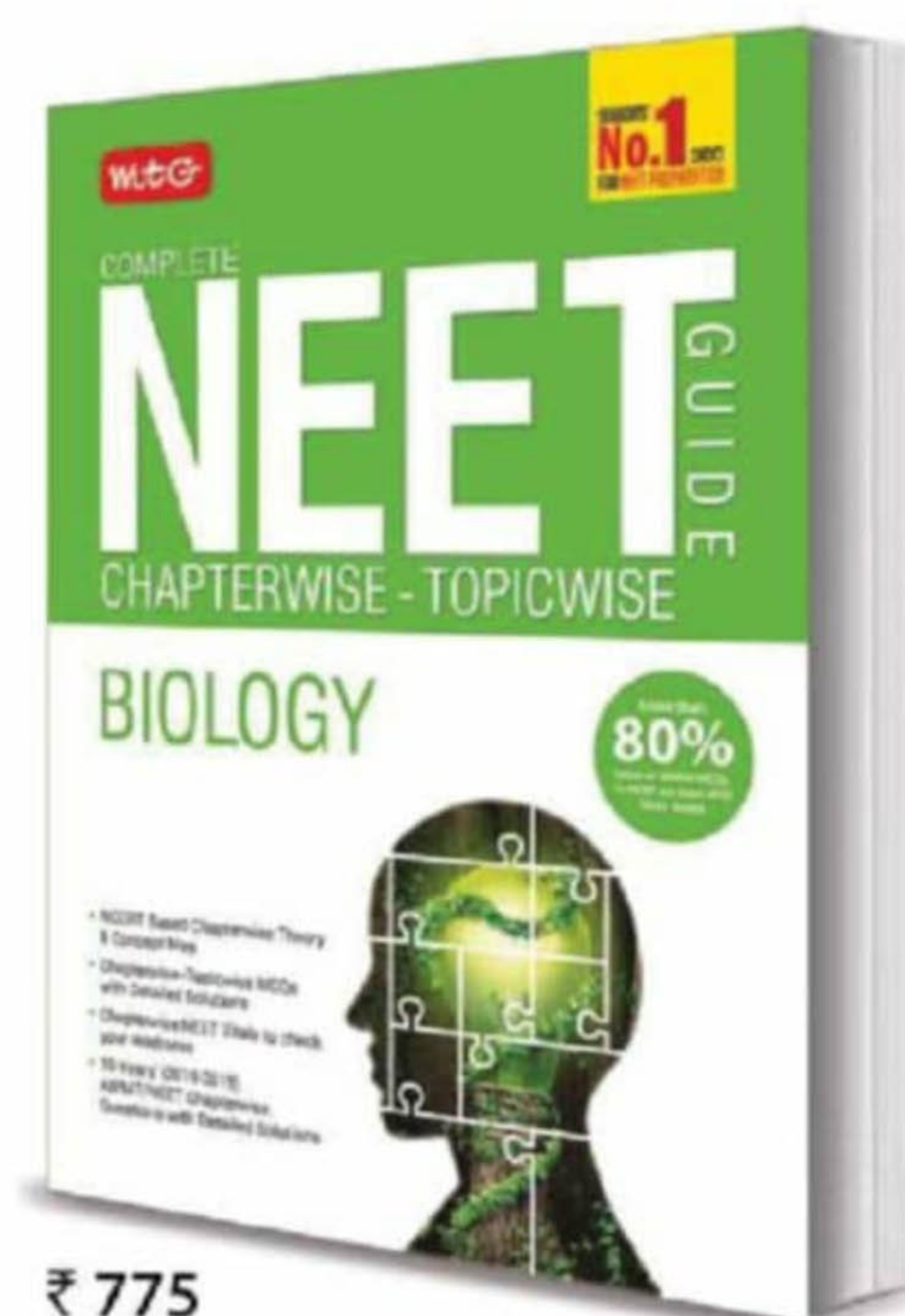
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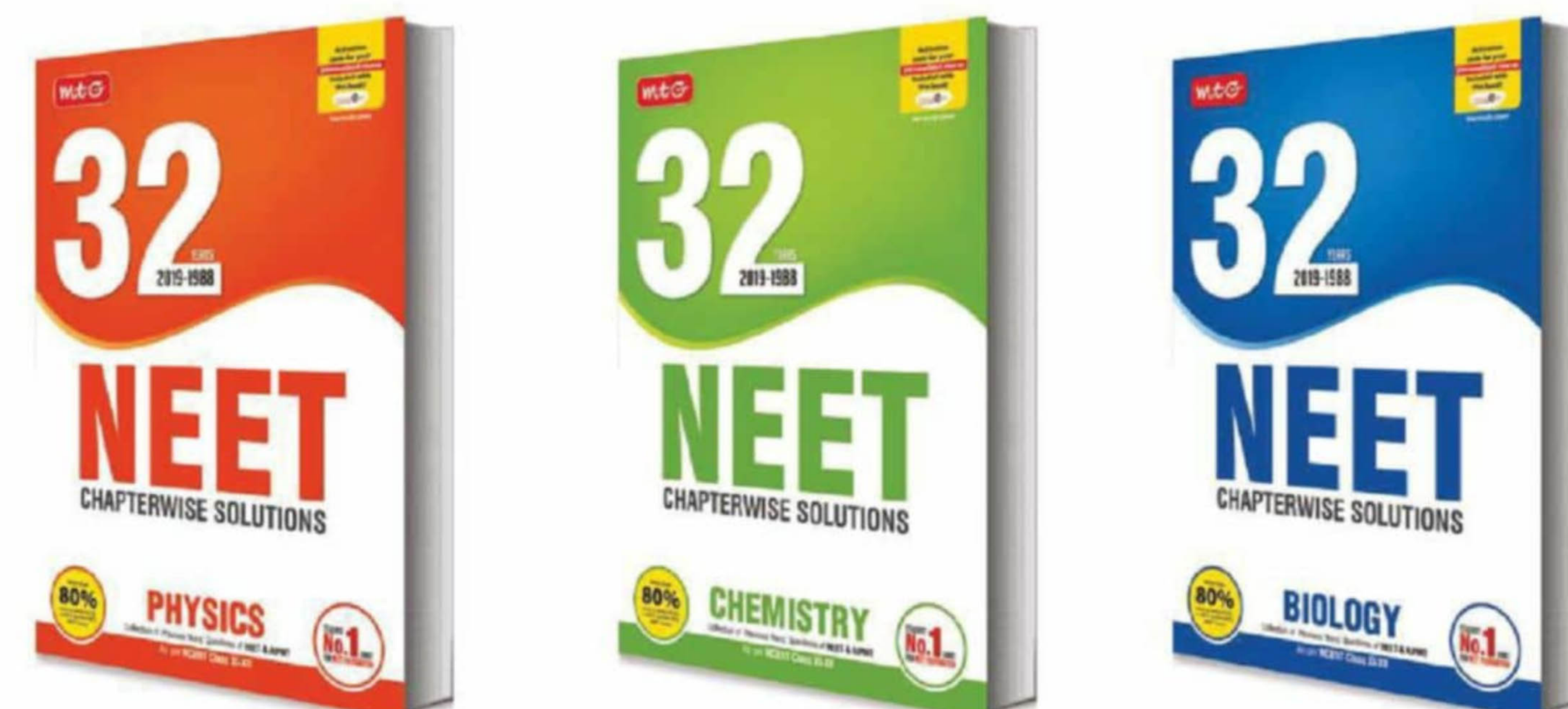
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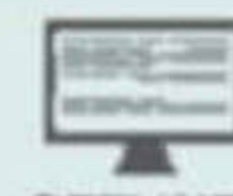
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